DUPLICATE

Title

STUDY OF THIN FILM LARGE AREA

PHOTOVOLTAIC SOLAR ENERGY CONVERTER

Third Quarterly Report, 1 Apr, 1963 - 30 Jun, 1963
April 1, 1963 - June 30, 1963

(NASA Contract No. NAS7-203)

National Aeronautics and Space Administration
Western Operations Office

(NASA CR-55738) OTS: $6.60 ph, $2.12 mf

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                        64p refs

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ABSTRACT

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This Third Quarterly Report discusses the work performed under Contract NAS7-203 during the period April 1, 1963 through June 30, 1963.

The effort expended on CdS solar cells during this quarter has been about evenly divided between evaporated films and single or multicrystals. Twelve evaporations were completed, yielding 210 individual film samples ranging in size from 1 in. x 2 in. to 4 in. x 4 in. in area. Fourteen single crystal photocells were prepared and thirty other crystal samples employed in various experiments.

Improvements in the evaporator are discussed along with optical and electrical measurements made on CdS films and film cells. Detailed descriptions are given of experiments performed on a film as it is processed into a photocell. These are: Optical transmission of the film before processing, after processing with the copper slurry, and after final heat treatment and formation of the barrier layer; spectral response of the completed cell; efficiency of the cell; and Hall effect and resistivity measurements on the film before processing. A similar set of data are presented for a single crystal cell.

Hall effect and resistivity data are given for a series of single crystal samples. These data are correlated with the optical transmission properties of the set of crystals.

It is pointed out that previously reported cell efficiencies were overestimated and a correction factor is given.

Progress in alternate methods of producing films and in film structure studies is dicussed. A detailed report of work done by the Mechanical Research Division, Clevite Corporation, is appended.

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1. INTRODUCTION

Present day photovoltaic solar energy converters are made of many small silicon cells, each of which must be soldered into a series-parallel array to provide the required electrical power for a given satellite system. A typical silicon cell is approximately 1 cm x 2 cm x 0.05 cm in size and has an efficiency of ten or fifteen percent; therefore, each cell delivers twenty or thirty milliwatts of power and many cells are required to power a satellite. Furthermore, each cell is very much thicker than its p-n junction; consequently, unnecessary weight is involved in a silicon solar cell array.

It is the purpose of this contract to develop a large area thin film photovoltaic solar energy converter. It is hoped eventually that cadmium sulfide cells one foot square and one or two mils thick will be produced, although for the present smaller areas will be studied. The highest efficiency of presently available thin film cadmium sulfide cells is around three percent over relatively small areas, and although the density of cadmium sulfide is twice that of silicon, the thickness of a cadmium sulfide cell is only about one-tenth that of a silicon cell. Thus, large area cadmium sulfide cells would compare favorably on a weight-per-watt and cost-per-watt basis with silicon cells. Furthermore, cadmium sulfide film cells have been produced on flexible metal and high-temperature organic plastic substrates, representing a great potential improvement over the rigid backing required by single crystal silicon cells.

This report covers work done during the third quarter of this contract.

2. EVAPORATED FILM CELLS

The effort expended on CdS solar cells during this quarter has been about evenly divided between evaporated film cells and single crystal cells.

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Twelve evaporations were completed, yielding 210 individual films ranging in size from 1 in. x 2 in. to 4 in. x 4 in. in area. Fourteen single crystal cells were prepared.

2.1 Evaporator

The double wall quartz crucible described in the Second Quarterly Report[1] has been improved by the addition of a tantalum heat shield which greatly reduces radiation losses and evaporator power. Four of these crucibles are installed in the 18-inch vacuum system. This evaporator is very fast; only seven to ten minutes are required to deposit films 0.0025 cm thick. Heretofore, only relatively large single crystal chips have been evaporated; when sintered material or powder is evaporated, spattering is excessive. Some experimenters have sought to reduce the amount of spattering by employing quartz wool plugs in their crucibles, but this reduces the evaporation rate so much that evaporation times as long as one hour have been reported.

The General Electric Co. manufactures a cloth woven from quartz fibers and it was decided to try this material for an evaporation of sintered CdS. Small patches were cut to fit into the open ends of the quartz crucibles forming a very thin plug. No spattering was observed and the evaporation time was only slightly longer than usual: twenty minutes evaporation yielded CdS films 0.004 cm thick. If this device proves successful in other evaporations, it will no longer be necessary to use single crystal chips. This represents a double advantage: it will not be necessary to wait for a crystal run to provide the charge for an evaporation; and it will not be necessary to "average out" the color of crystal chips making up the charge in each crucible. It is well known that the distribution of dopant in a crystal boule is not uniform, whereas it is uniform in the sintered CdS used as the starting material for a crystal growth run.

Another development under way, and just about ready to try, is a heated pyrex cylinder enclosing the evaporator and substrate. This is presently assembled in the 12-inch vacuum system. A single quartz crucible is located in a hole in the bottom of a three-liter pyrex beaker. The lip and spout of

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the beaker have been removed. The substrate, its holder and heater are located just above the upper edge of the beaker. This entire assembly is surrounded by a pyrex cylinder made by cutting off the lip, spout and bottom of a four-liter beaker. A tungsten wire heater is wrapped around this outer cylinder. It is anticipated that during evaporation the inner beaker will be heated by the outer beaker and its temperature maintained a little above that of the substrate. The inner beaker, crucible and substrate form an essentially closed system within the vacuum system, and it is expected that little or no CdS vapor will escape from the inner chamber. It is further expected that the CdS vapor will condense only on the substrate, which will be the coolest part of the inner chamber. This should greatly increase the efficiency of evaporation which heretofore has been rather low, e.g., 5 to 8 gm of CdS deposited from a charge weighing 40 gm. It is further expected that the stoichiometry of the evaporated CdS will improve.

2.2 Evaporant

Five crystal boules provided the evaporant for all the evaporation runs completed during this quarter. Boules T-5 and T-6 were grown by the method described in the Second Quarterly Report[1] and doped with 0.05 and 0.1 mol percent indium respectively. Boule T-7, doped with 0.05 mol percent indium, failed to grow completely when all of the sinter failed to transfer. As a result, the actual doping level of the crystals was probably somewhat lower than planned while the remaining sinter was probably more heavily doped. Boule T-8 was grown from the remaining sinter of boule T-7 plus a sinter of undoped CdS. The two sinters were placed side by side in the growth tube, the undoped sinter on the left and the doped sinter on the right. This presented an interesting situation in crystal growing. The obvious question arose whether the crystal grown at the left end, adjacent to the undoped sinter, would contain no indium or approximately half the concentration of indium initially in the doped sinter; i.e., would the indium distribute itself uniformly? When the crystals were removed from the growth tube, it was found that indium had indeed transferred across the undoped sinter and into the left crystal, but the distribution was not uniform. The left hand crystal contained

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much less indium than the right hand crystal. Boule T-9 doped with 0.005 mol percent indium was grown in the usual manner.

The discussion of the next section will point up the difficulties resulting from the nonuniform distribution of dopant that invariably occurs when crystal boules are grown from the vapor phase. Indeed, this nonuniformity is undoubtedly the worst stumbling block of this entire project, for it is impossible to predict the outcome of an evaporation when the composition of the evaporant varies so widely.

On the other hand, the composition of the sintered material is known and is uniform throughout the sinter. Therefore, if the employment of quartz cloth plugs in the evaporator continues to be successful, sintered, doped CdS can be evaporated instead of crystal chips, and a very important gain in control of evaporation parameters will have been achieved.

2.3 Production of Films

Parameters including substrate distance, evaporation temperature and substrate temperature were adjusted such that a 25 micron thick deposit of CdS was obtained in six to seven minutes of evaporation. The substrate cleaning procedure was improved by boiling the glass substrates in several changes of distilled water after washing with Alconox detergent.

Evaporations 23 through 27 were made from crystal boules T-5 and T-6. The areas of the cells obtained ranged from 18.8 cm^2 to 2.8 cm^2 with the average cell having 7.8 cm^2 of area. The photovoltaic efficiencies of these cells ranged from 1.8 percent to less than 0.5 percent: six cells had efficiencies between 1.5 and 1.8 percent, eight cells were between 1.0 and 1.3 percent, four cells were between 0.7 and 0.9 percent, five cells were between 0.5 and 0.6 percent, and two cells were below 0.5 percent efficient. The better cells were obtained from run 25, which was evaporated from light colored chips of boule T-5. The others runs were made from the dark chips of T-5 and from T-6 which had twice the indium content of T-5.

Run 28 was made from boule T-6; run 29 was made from boule T-7 which, as mentioned in Section 2.2, involved incomplete transfer of the sinter during crystal growth. Run 30 was made from some of the crystal chips and untrans-

ferred sinter of boule T-7.

Run 28 was badly contaminated with aluminum evaporated from the shutter and base plate cover. The heat shields around the new quartz crucibles so concentrated the heat that the temperature of aluminum foil on the shutter assembly was raised to the evaporation point during the outgassing step. Aluminum was evaporated into the crucibles containing the CdS charge and upon opening the shutter was coevaporated with the CdS. None of this could be observed during the evaporation, but the circumstances were easily reconstructed after examining the apparatus and evaporated films. The situation was corrected by simply increasing the distance between the crucibles and shutter and eliminating the aluminum foil. Subsequent processing of the films resulted in photovoltaic cells with fairly good open circuit voltages but very low efficiencies.

Run 29 was made from a charge of dark colored, low resistance CdS from the last grown end of boule T-7. Presumably this is the end containing the greater portion of the indium dopant. The films exhibited very low resistance and efficiencies less than one percent. For run 30, the charge was composed of a mixture of light and dark colored CdS crystal chips from T-7, in an attempt to lower the net indium concentration in the deposit and increase its resistance. Again the resulting cells were low in resistance and less than one percent efficient, showing that the ratio of light to dark chips was too low.

Evaporation run 31 was evaporated from the left hand crystal of boule T-8, i.e., the crystal grown nearest the undoped sinter in the growth tube. The films exhibited high resistance, 2000 to 3000 ohms, and the resulting cells were low in efficiency although good open circuit voltages were obtained. Run 32 was evaporated from the right hand or heavily doped crystal of boule T-8. The film resistance was in excess of 200,000 ohms, and the films were completely unsuitable for cells. It is not understood why this heavily doped material yielded high resistance films.

Evaporation run 33 was made from sinter T-9, doped 0.005 mol percent indium. This was the first attempt using the quartz cloth to restrict spattering from sintered material. The films showed no evidence of spattering, indicating the success of the quartz cloth, but again the resistance was high, in excess

of 200,000 ohms. This is probably due to the low indium content of the sinter. There is evidence that good films require a doping level (in the evaporant) of 0.01 to 0.05 mol percent, as is the case with boule T-5, which produced runs 21 and 25, yielding the best film cells. Carrier concentration measurements on these films are in the process of being made, and preliminary data support this idea.

Run 34 was evaporated from sinter T-5, again using the quartz cloth plugs. The films have not yet been processed into cells, but they have resistances in the proper range of 10 to 50 ohms, show good adherence and no spatter.

It is now apparent that a chemical reaction occurs almost immediately upon application of the copper slurry to the doped cadmium sulfide film (or crystal). This reaction takes place at room temperature and is manifested by a darkening of the area of contact. Photovoltaic activity is generally observed after heating the treated cadmium sulfide on a 300°C hot plate for a few seconds. The darkened layer is believed to be p-type Cu_2S, and it is strongly suspected that the reaction involves chloride, nitrate and cuprous ions present in small quantities in the slurry. It is also suspected that the relative amounts of these species influence such cell properties as short circuit current, open circuit voltage and rectification.

A few cells were provided with evaporated gold collector electrodes. Some were partially or completely shorted, and it is believed that this is due to incomplete wetting or reaction of the CdS with the slurry. Forcing the reaction by heating the slurry coated CdS to 70°-80°C for a few minutes while preventing drying of the slurry improved this situation.

The efficiency of a film cell appears to decrease as the area is increased beyond about one inch square. This is probably due to the series resistance of the CdS layer which serves as the transparent electrode in the backwall cell. An improvement in film cell efficiency is expected if a 1 x 1 inch grid of evaporated silver or gold is placed on the substrate before evaporating the CdS layer. The width of the conductors in this grid would be about one-half millimeter.

It has become evident that an improvement in film cell efficiency is obtained by reducing the concentration of indium dopant in the charge. It was

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tentatively hypothesized that the observed increase in open circuit voltage was due to this lower indium concentration and that it more than compensated for the increase in sheet resistance, resulting in the increased efficiency. Most of the evaporations made during this quarter support this hypothesis.

3. SINGLE CRYSTAL CELLS

Single crystal cells have been prepared from time to time in order to provide comparison criteria for evaporated film cells. In order to obtain a convenient supply of single crystals, it has become customary to grow half inch diameter CdS cylindrical crystals along with the large crystalline boules used as the evaporant for the film cells. This is accomplished easily because the crystal growth process employed by this laboratory ordinarily produces two large crystal boules, one at each end of the growth tube. These boules are grown in quartz cups which closely fit the ends of the growth tube and are one inch or more in diameter, depending on the diameter of the growth tube. To obtain the smaller diameter crystals, it is only necessary to replace one of the cups with a number of half-inch and quarter-inch diameter quartz tubes. Thus each crystal growth run yields one large diameter CdS crystal boule and a number of half- or quarter-inch diameter crystal boules.

Boules T-5, T-6 and T-8 each produced a number of these small CdS cylindrical crystals.

Some of the crystals from each run were sliced into discs one half inch in diameter and one or two millimeters thick. Some of the discs were processed into photovoltaic cells directly, others were used for optical transmission measurements, Hall effect measurements and conductivity measurements. These will eventually be processed into photovoltaic cells. So far, about thirty discs have been obtained for these measurements. Each must be lapped flat and parallel and polished for the transmission measurements. Then each must be electroded for the electrical measurements; these electrodes must be removed and the crystals re-etched before they can be processed into photocells. Then they must be electroded again and measurements made of conversion efficiency, spectral response, diode characteristics and barrier layer capacitance.

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Most of the transmission measurements have been completed and some of the discs have been processed into cells. It will be some time yet before this set of measurements is completed, but it is anticipated that the data obtained will go a long way toward disclosing the nature of the barrier layer and the details of the photovoltaic process in films. Similar measurements will be made on films and film cells in order to correlate their properties with the crystal cells.

One set of six discs from boule T-5 was processed into photocells without performing any other measurements. Each disc was a different shade of yellow, indicating a different level of indium doping. Two specimens, 1.7 cm apart on the bar, showed a 3.75 to 1 ratio of efficiencies, the lighter yellow wafer having the higher efficiency.

The efficiencies of two other cells from this bar were measured under varying intensities of illumination. One cell, 28T-5, showed a relatively constant efficiency as the light intensity was varied from 25 to 125 mW-cm^{-2}; the other, 26T-5, showed an increase in efficiency with an increase in intensity. The short circuit current of 28T-5 varied linearly with light intensity, while the variable efficiency cell showed a short circuit current increasing faster than linear. These data are shown in Fig. 3-1. The open circuit voltage of cell 28T-5 increased with light intensity, while the open circuit voltage of Cell 26T-5 was essentially constant. Furthermore, the first quadrant dynamic resistance of cell 28T-5 was constant at 1.8 ohms for the various light intensities, while that of cell 26T-5 decreased from about 3.6 ohms to 1.7 ohms.

Eight other single or multicrystal cells were prepared to examine the effects of electroding and the presence of grain boundaries. The efficiencies ranged from about 1 to 6.7 percent. The one percent cell had an evaporated gold collector electrode. The data are too scattered, however, to allow conclusions concerning grain boundaries.

4. MEASUREMENTS

4.1 Hall Effect and Resistivity

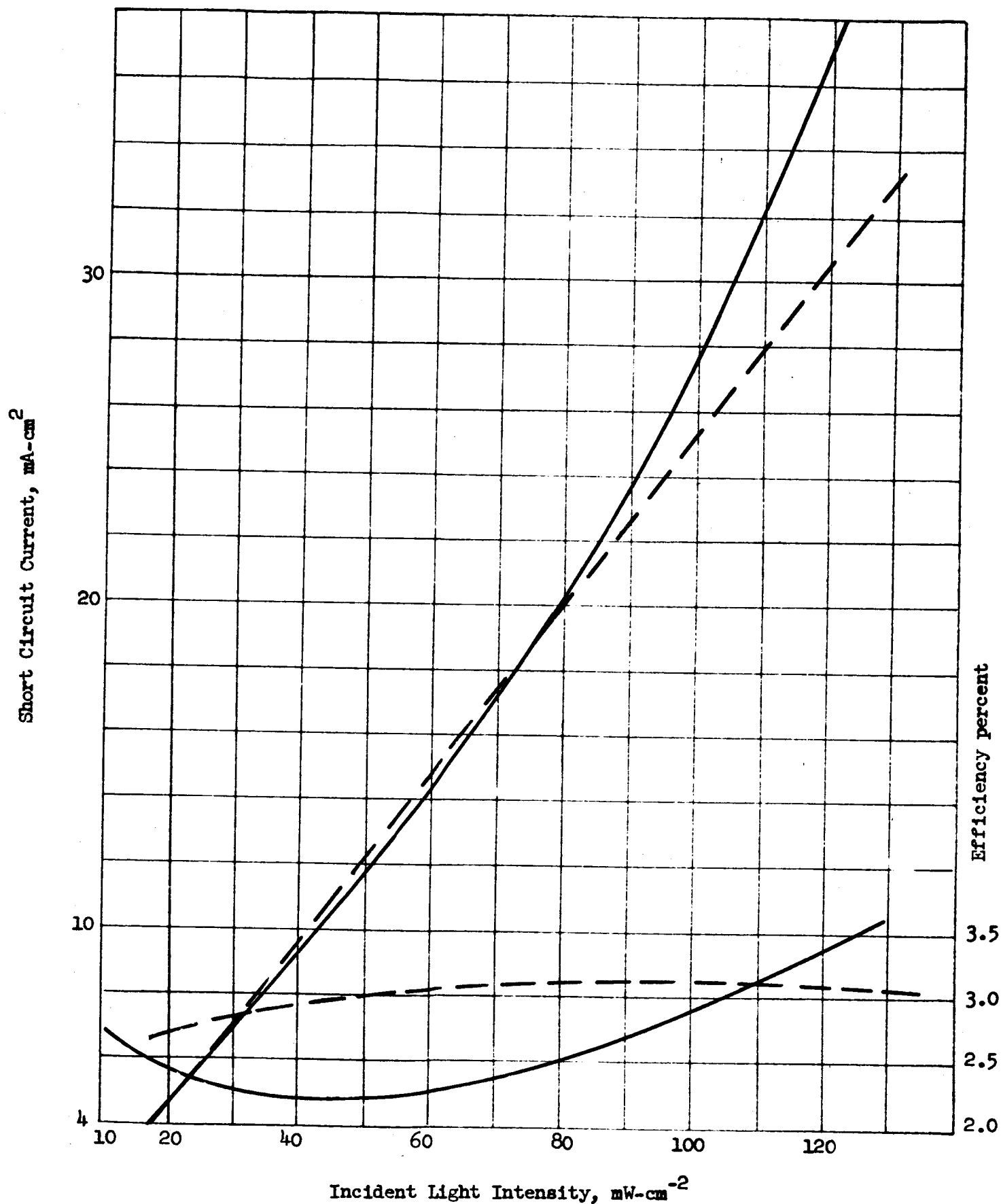The Hall coefficient and resistivity of a number of evaporated films have

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Figure 3-1. Variation of Short Circuit Current and Efficiency with Incident
Light Intensity. Solid Curve - Crystal Cell 26T-5. Dashed
Curve - Crystal Cell 28T-5.

been determined. Some experimental problems such as electrical contacts to the films and a fixture to hold the films were encountered and eventually solved. A special mask was constructed to fit over one of the 1 in. x 2 in. glass substrates to yield a film with a suitable shape for Hall measurements. However, this is not always desirable, so an experimental set-up has been evolved to employ the van der Pauw[2] method of measuring Hall effect and resistivity. This technique is also employed on crystal discs. Only four ohmic contacts to the sample are required instead of five or seven as in the conventional measurement. The implicit assumption of uniform resistivity in the sample is not always met, but the errors incurred are usually small. The results for four film samples are given in Table 4-1.

TABLE 4-1. Electrical Properties of CdS Evaporated Films

Film No.	Resistivity, ohm-cm	Carrier Concentration, n, cm^{-3}	Mobility, $cm^2 volt^{-1} sec^{-1}$	Film Thickness, cm
16-2-A	0.0121	2.9×10^{19}	18.1	.00381
21-3-E	0.0293	8.04×10^{18}	26.5	.00279
25-1-A	0.0523	8.55×10^{18}	14	.00305
27-2-C	0.0132	6.42×10^{19}	7.40	.00405

These data are insufficient to correlate with photovoltaic properties, but it is interesting to note that film No. 21-3-E, exhibiting the highest mobility, is from the same evaporation that yielded high efficiency film cells.

Many more films are being measured and will be reported on in the next report.

Table 4-2 lists the results for a set of single crystal samples. These are half-inch diameter discs cut from two bars of boule T-6. One of these bars, T6-1, gave a good selection of flawless, light yellow discs, while bar T6-2 gave a selection of relatively flawless, dark discs. No data are given for the first and fourth discs of either bar. The first discs, being the heads

TABLE 4-2. Electrical Properties of CdS Crystals

Disc No.	Resistivity, ohm-cm	Carrier Concentration, n, cm^{-3}	Mobility, $cm^2 volt^{-1} sec^{-1}$
T6-1-1	-	-	-
T6-1-2	0.0563	5.11×10^{17}	217.6
T6-1-3	0.0493	4.79×10^{17}	274.1
T6-1-4	-	-	-
T6-1-5	0.0558	4.3×10^{17}	312.5
T6-1-6	0.0415	6.03×10^{17}	250.8
T6-1-7	0.0264	0.99×10^{18}	240.0
T6-1-8	0.0196	1.30×10^{18}	246.5
T6-1-9	0.0129	2.47×10^{18}	198.0
T6-1-10	0.0072	4.15×10^{18}	209.0
T6-2-1	-	-	-
T6-2-2	0.0105	3.17×10^{18}	189.2
T6-2-3	0.0093	3.27×10^{18}	216.4
T6-2-4	-	-	-
T6-2-5	0.0039	1.17×10^{19}	135.5
T6-2-6	0.0034	1.04×10^{19}	181.0
T6-2-7	0.0027	1.16×10^{19}	203.3

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of the bars, were curved and exhibited flaws. The fourth discs of each bar, which were really quite thick (perhaps 5 mm), included the relatively sharp but badly flawed boundary between the light and dark CdS and shattered as the saw cut through. Although these samples are called discs, not all of them are complete discs. All the samples from bar T6-1 were either complete discs or large sections of discs. Of the samples from T6-2, only "discs" 2, 6 and 7 were large enough sections of discs to be used later in optical transmission measurements; 3 and 5 were very irregularly shaped. This points up the advantage of the van der Pauw measurement technique which does not require a regularly shaped sample.

The numbering of discs corresponds with their position along the crystal rod. The first grown end of the bar, numbered 1, is also the lightest in color. The color deepens as one traverses the bar from the first grown end to the last, from disc No. 1 to disc No. 7 or 10. It is apparent from the data in Table 4-2 that the carrier concentration increases as one goes to the last grown (dark) end of the bar, while the mobility decreases. If one assumes that the carrier concentration is solely a function of indium content, it is a simple matter to calculate the indium concentration corresponding to the maximum and minimum carrier concentrations listed in Table 4-2. These are 0.05 mol percent and 0.002 mol percent indium, respectively, for the dark and light discs. The boule from which the samples were obtained was grown from a sinter containing 0.1 mol percent indium. Thus it would appear that only half the indium was carried over into the boule, and since experience indicates that yellow crystals make better photocells than dark crystals, very little indium is required in CdS for good crystal cells. This is in general agreement with the hypothesis discussed in Section 2.3 in connection with film cells.

As yet, very little is known about the amount of indium carried over into evaporated films. It is planned to investigate this further with radioactive indium tracer measurements. Pieces of crystal CdS heavily doped with radioactive indium are now available in this laboratory. Some of these will be employed as the charge in an evaporation. Measurements will be made to determine how much indium goes into the film, how much stays in the unevaporated portion of the charge and how much deposits elsewhere in the vacuum system. This in-

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formation, and the information to be obtained from Hall effect and resistivity measurements on my films, should permit a correlation among cell quality, indium content and carrier concentration. It must not be forgotten that some or perhaps most of the conductivity observed in these CdS crystals and films might be due to excess cadmium.

4.2 Optical Measurements

The following discussion represents the complete history of a film cell. This cell was taken from evaporation run 21. Figure 4-1 shows the optical transmission relative to air of CdS film 21-3-H. Curve 1 is the transmission of the film as removed from the vacuum system. Curve 2 shows the transmission of the film after the copper slurry was applied and washed off but before the final heat treatment. Curve 3 shows the transmission of the film after the final heat treatment and formation of the barrier layer. At this point the photovoltaic cell is complete except for the two electrodes, one of which will be a silver paint electrode covering the processed area of the cell. The fact that curves 2 and 3 are essentially the same shows that the final heat treatment does not produce any change in the spectral transmission. One might be tempted to claim that the barrier layer is formed upon application of the slurry and low temperature heat treatment, and that the final heat treatment is not essential. In a sense this is true, for some photovoltaic activity has been observed after the low temperature heat treatment, but good cells have never been obtained without the high temperature heat treatment.

Figure 4-2 shows the current-voltage characteristic of photovoltaic film cell 21-3-H. The efficiency was measured to be 1.1 percent. This is considerably lower than the efficiencies of other cells made from the same evaporation. One such cell, located within four inches of 21-3-H on the substrate holder, had an efficiency of 3.1 percent.
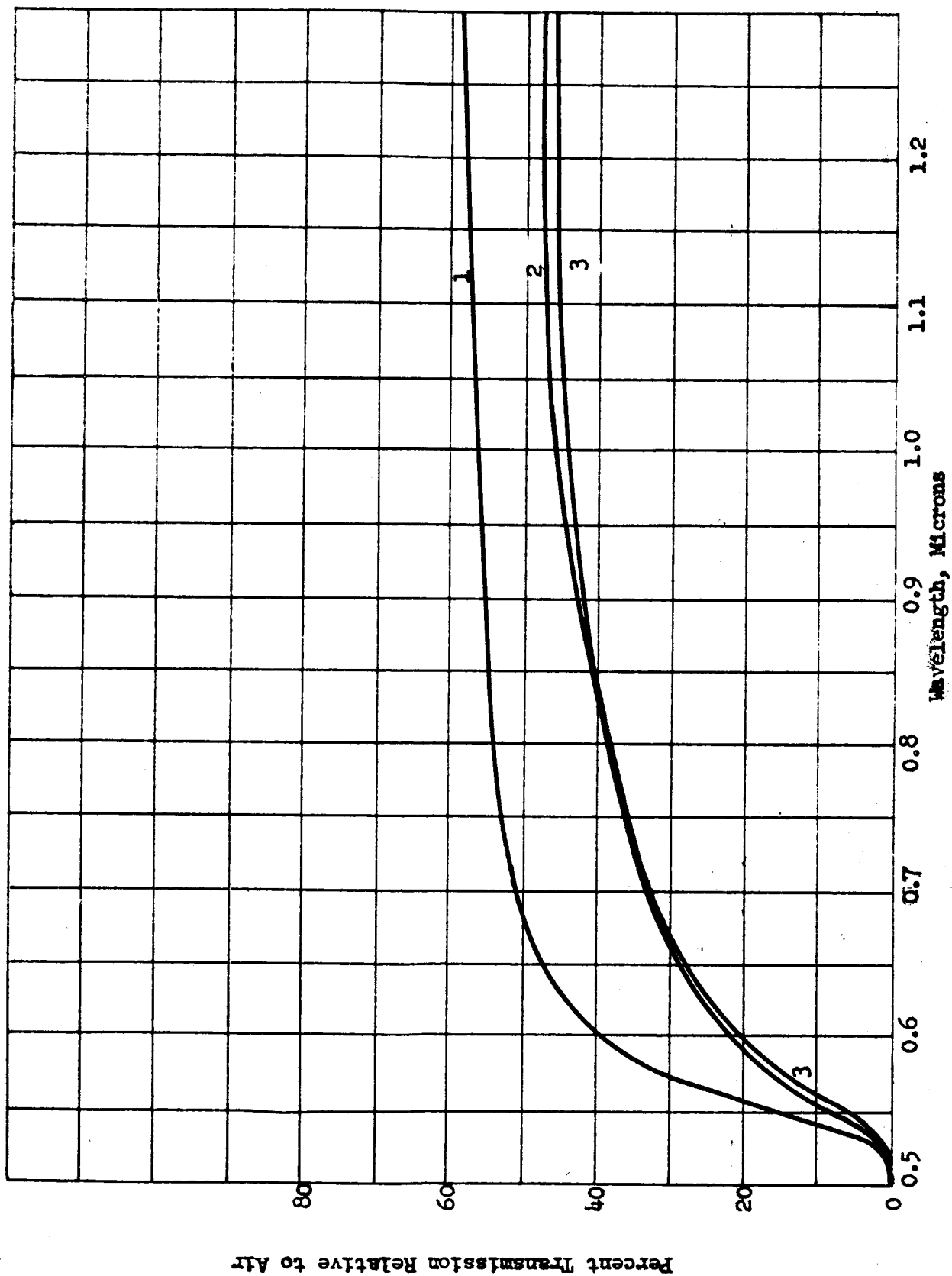
Figure 4-1. Spectral Transmission of Evaporated CdS Film 21-3-H.
Curve 1: Untreated.
Curve 2: Copper Slurry Applied and Washed Off.
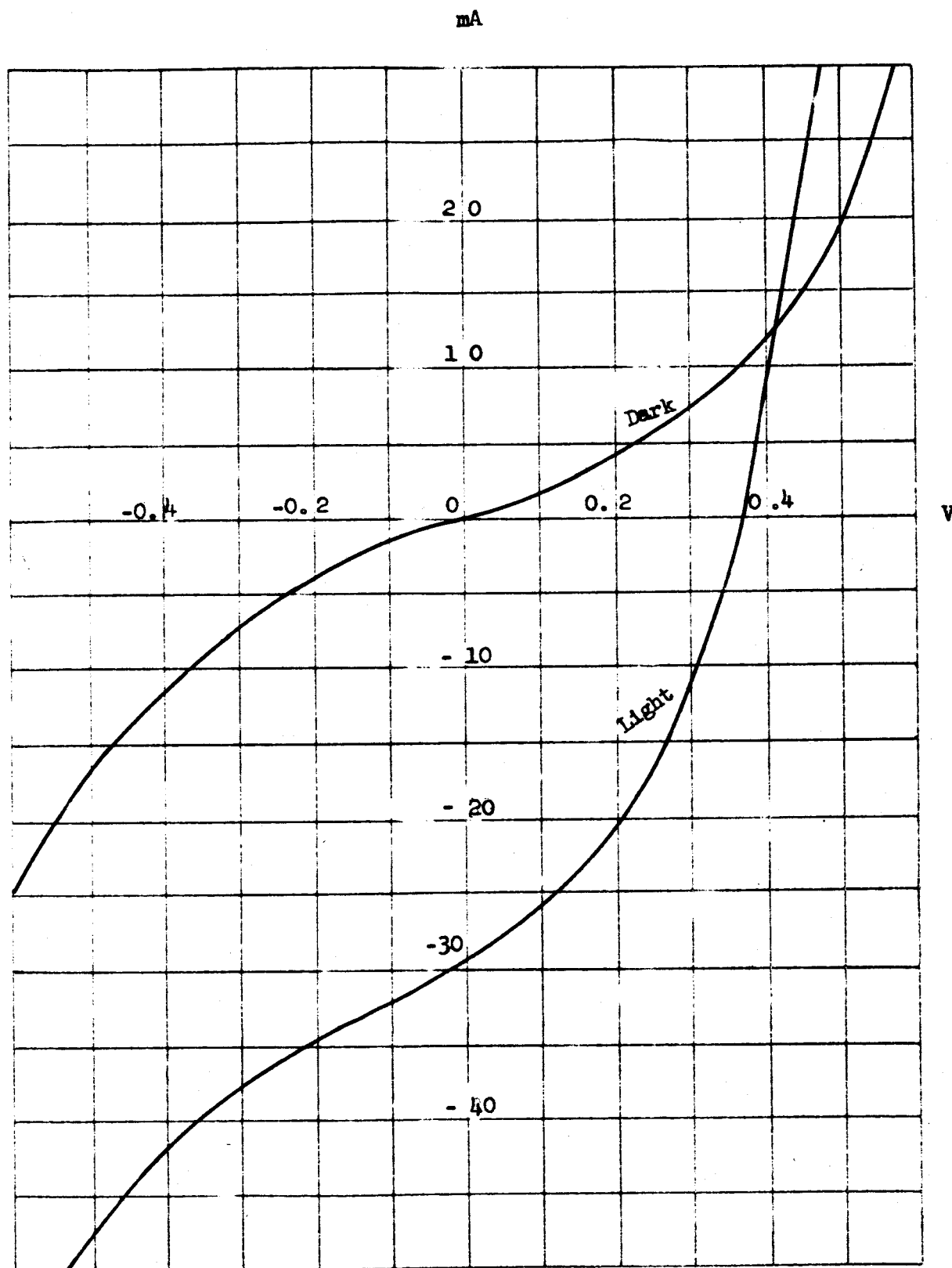Curve 3: Processed Completely.

Figure 4-2. Current-Voltage Characteristic of Evaporated CdS Film Cell 21-3-H.
Active Area: 2.79 cm^2. Efficiency: 1.1%.

It was not possible to measure the Hall coefficient and resistivity of film 21-3-H for this would require destruction of the cell. These measurements were made on film 21-3-E, located within two inches of 21-3-H. The data (also given in Table 4-1) are: resistivity, 0.029 ohm-cm; carrier concentration, n, 8.04×10^{18} cm^{-3}; mobility, 26.5 cm^2 volt^{-1} sec^{-1}; and thickness, 0.00279 cm. The active area of photovoltaic cell 21-3-H was 2.79 cm^2.

The spectral response of cell 21-3-H is shown in Fig. 4-3. The lower curve is uncorrected for the variation, with wavelength setting, of the monochromator output intensity. If it is assumed that (at least at the low light levels available from the monochromator) the response of the cell is independent of intensity at a given wavelength, the upper curve of Fig. 4-3 can be calculated. This curve shows the response of the cell for equal incident light intensity at each wavelength. Figure 4-4 shows the spectral response for a constant number of photons (3.76×10^{14} cm^{-2}sec^{-1}) incident at each wavelength. On the same figure is shown the number of photons required to generate one electron of short circuit current (hole current is assumed to be zero) at each wavelength. At the wavelength corresponding to the peak response of the cell, about 0.054 electrons are obtained for each incident monochromatic photon. This is the unenhanced response. With light bias, illuminating the cell with a constant white or red light in addition to the monochromator radiation, the number of electrons per photon would be increased by a factor of 10 or more.[3]

A similar history has been obtained for a single crystal cell. The optical transmission of CdS crystal cell 31-T-5-7 is shown in Fig. 4-5. The upper curve is the transmission of the disc after lapping its faces flat and parallel and optically polishing them. The lower curve is the transmission after etching one face in HCl. The etched face is the sulfur rich face, about which a more detailed discussion will be given below. There was no appreciable change in the transmission after processing. Hall coefficient and resistivity measurements were not made on this disc.

Comparing Figs. 4-5 and 4-1, it is seen that the slope of the transmission curve of the crystal at the absorption edge is much steeper than that of the film. Some of this change may possibly be attributed to the difference in thick-

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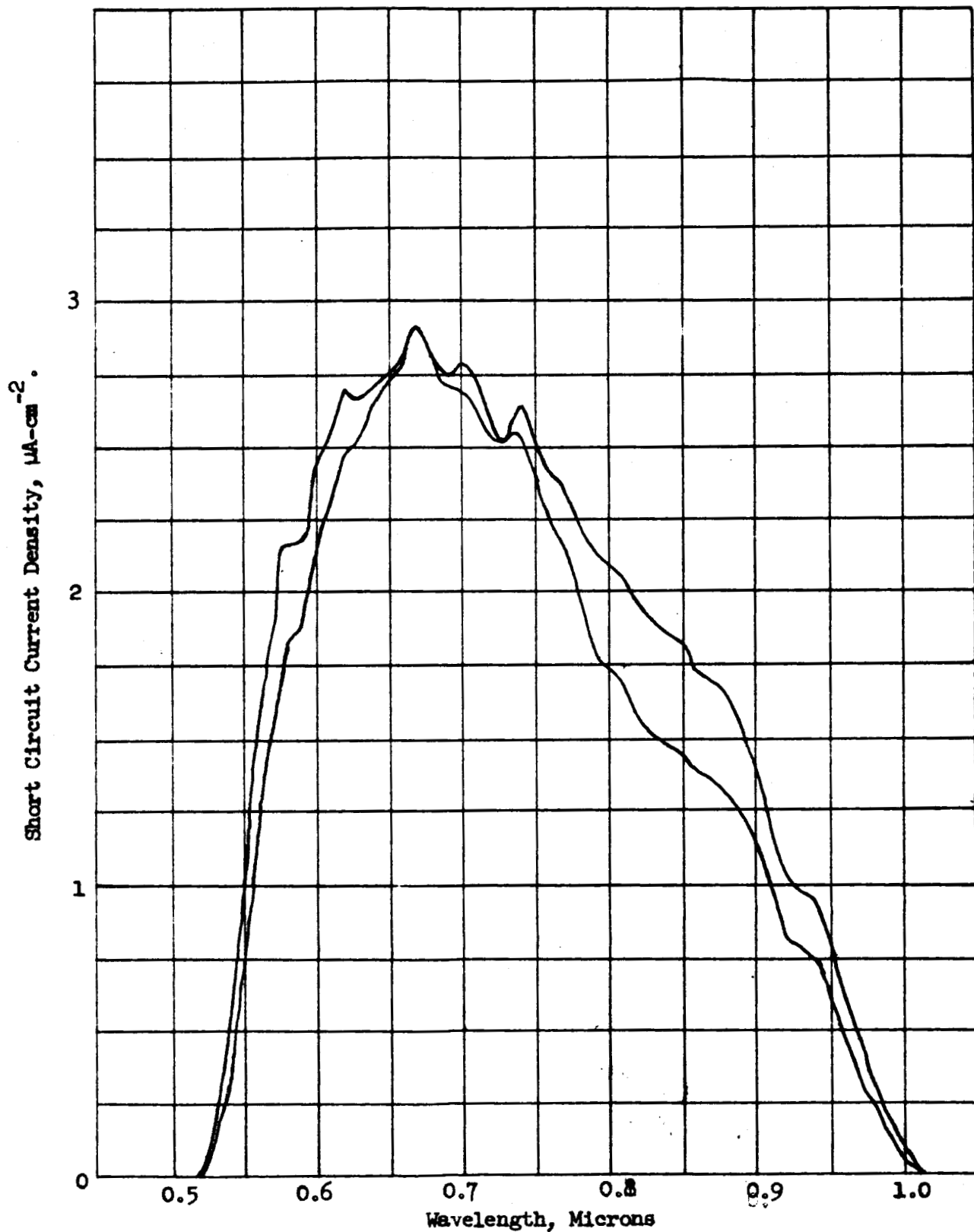
Figure 4-3. Spectral Response of CdS Film Cell 21-3-H.
Upper Curve: Corrected for Constant Energy Input.
Lower Curve: Uncorrected.

Figure 4-4. Spectral Response of CdS Film Cell 21-3-H for Constant Number of Photons Incident per Unit Area per Unit Time. Number of Photons Incident = 3.76×10^{14} photons-cm^{-2}-sec^{-1}. Solid Curve Is Spectral Response. Dashed Curve Is Number of Photons Required to Produce One Electron.

Figure 4-5. Spectral Transmission of Single Crystal CdS Disc. 3175-7

Lower Curve: After Etching One Face

PERCENT TRANSMISSION

WAVELENGTH, MICRONS

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ness of the two samples. The disc is 0.1467 cm thick while the film is only 0.00279 cm thick. This probably also accounts for the difference in the long wavelength transmission. There is a considerable difference in the slopes of the curves for the processed samples. Again the difference may be attributed to the thickness and to the deeper etch given to the crystal.

The disc was processed into a photovoltaic cell. Its efficiency was 3 percent and active area was 1.0 cm^2. Its spectral response for a constant number of photons (5.23×10^{14} cm^{-2} sec^{-1}) incident at each wavelength is shown in Fig. 4-6. Again, the dashed curve shows the number of photons required to generate one electron of short circuit current. There is a distinct difference in the response curves of the two cells (Fig. 4-4 and Fig. 4-6), and at the wavelength corresponding to peak response, about 0.33 electrons are obtained for each incident photon. This is more than six times the response of the film cell. Again, this is the unenhanced response.

It was mentioned in Section 3 that optical transmission measurements were made on a number of single crystal discs cut from half-inch diameter, single crystal, cylindrical boules. These boules are naturally oriented with the c-axis approximately parallel to the cylinder axis. The structure of CdS is such that as one traverses a crystal along the c-axis, one encounters layers of cadmium atoms alternating with layers of sulfur atoms. This gives rise to different rates of etching on the plus (cadmium rich) and minus (sulfur rich) faces of a c-cut crystal. There is also a different etch pattern on the two faces. One face, the sulfur rich face, has larger etch pits and exhibits a matte surface. The other face is smooth and shiny. It has been general practice to put the barrier layer on the matte surface because it is easier to wet with the slurry. As shown in Fig. 4-5, an etched crystal is very efficient in stopping light. This is probably due to a combination of scattering and total reflection by the sides of the etch pits. Polishing the etched face resotres the transmission to the upper curve. Furthermore, this effect is independent of the direction of light through the disc. If both faces are etched, the transmission is reduced even more than if only the matte face is etched.

The optical transmission relative to air of the discs listed in Table 4-2 has been measured. Excepted are discs T6-2-3 and T6-2-5, which were too small.
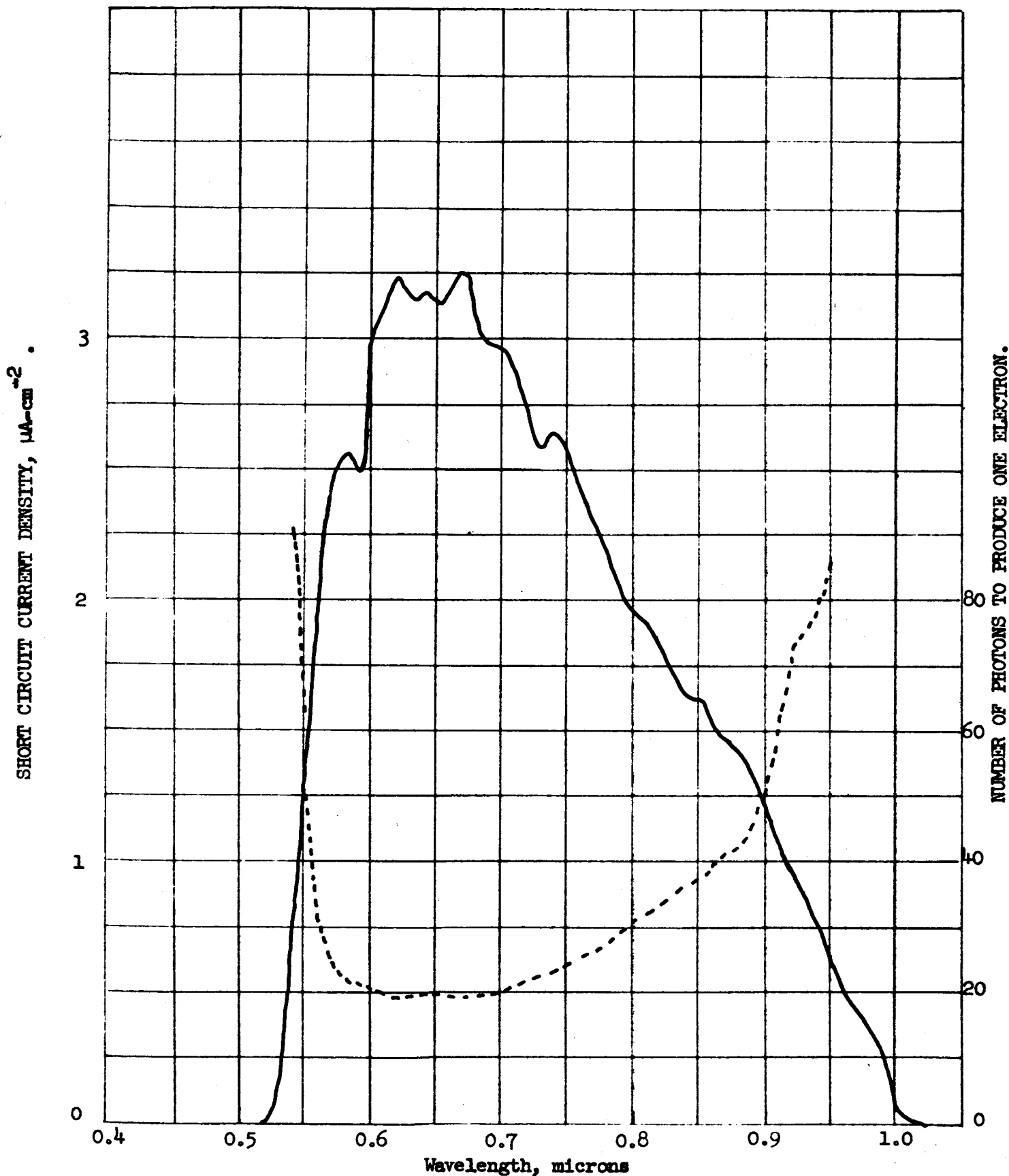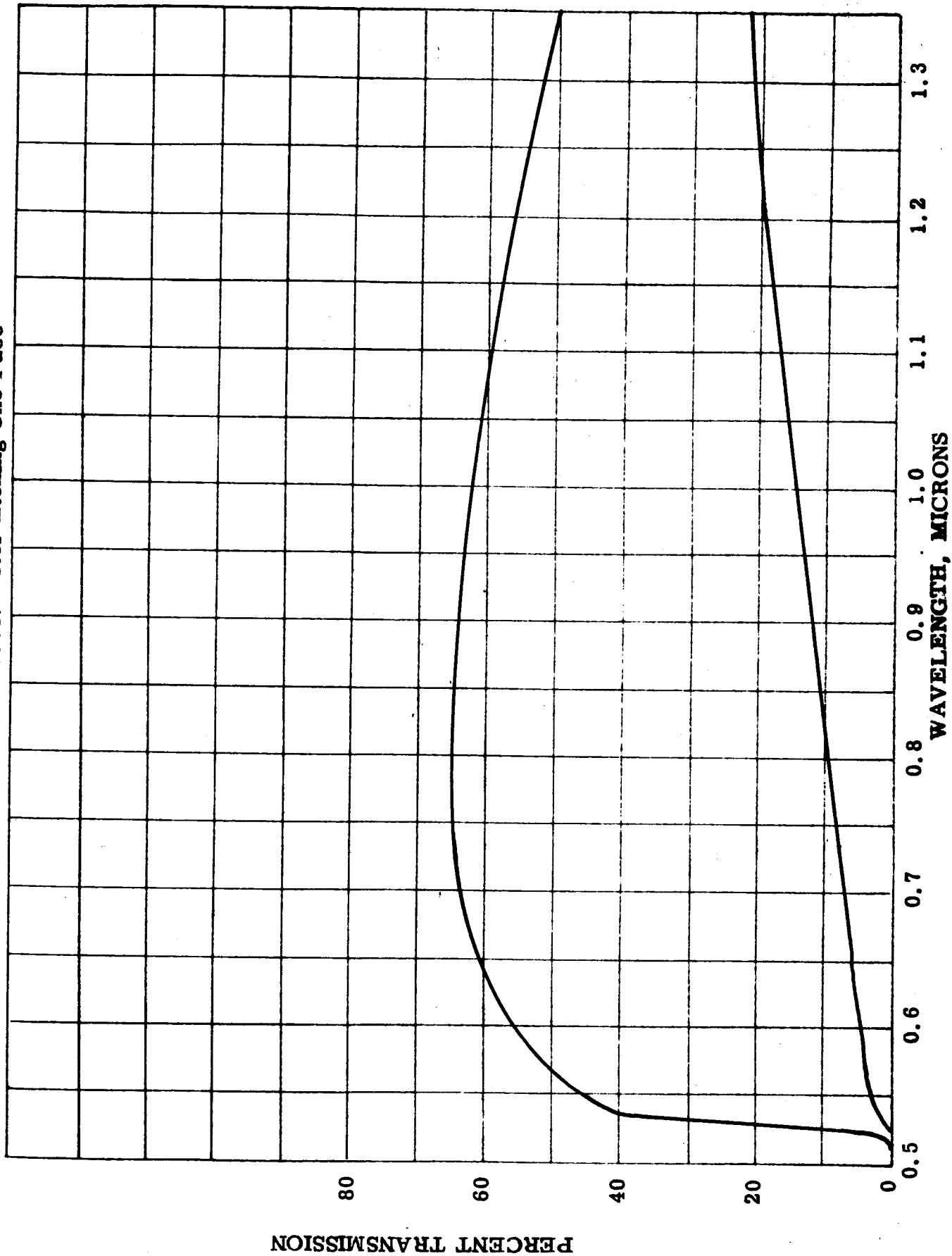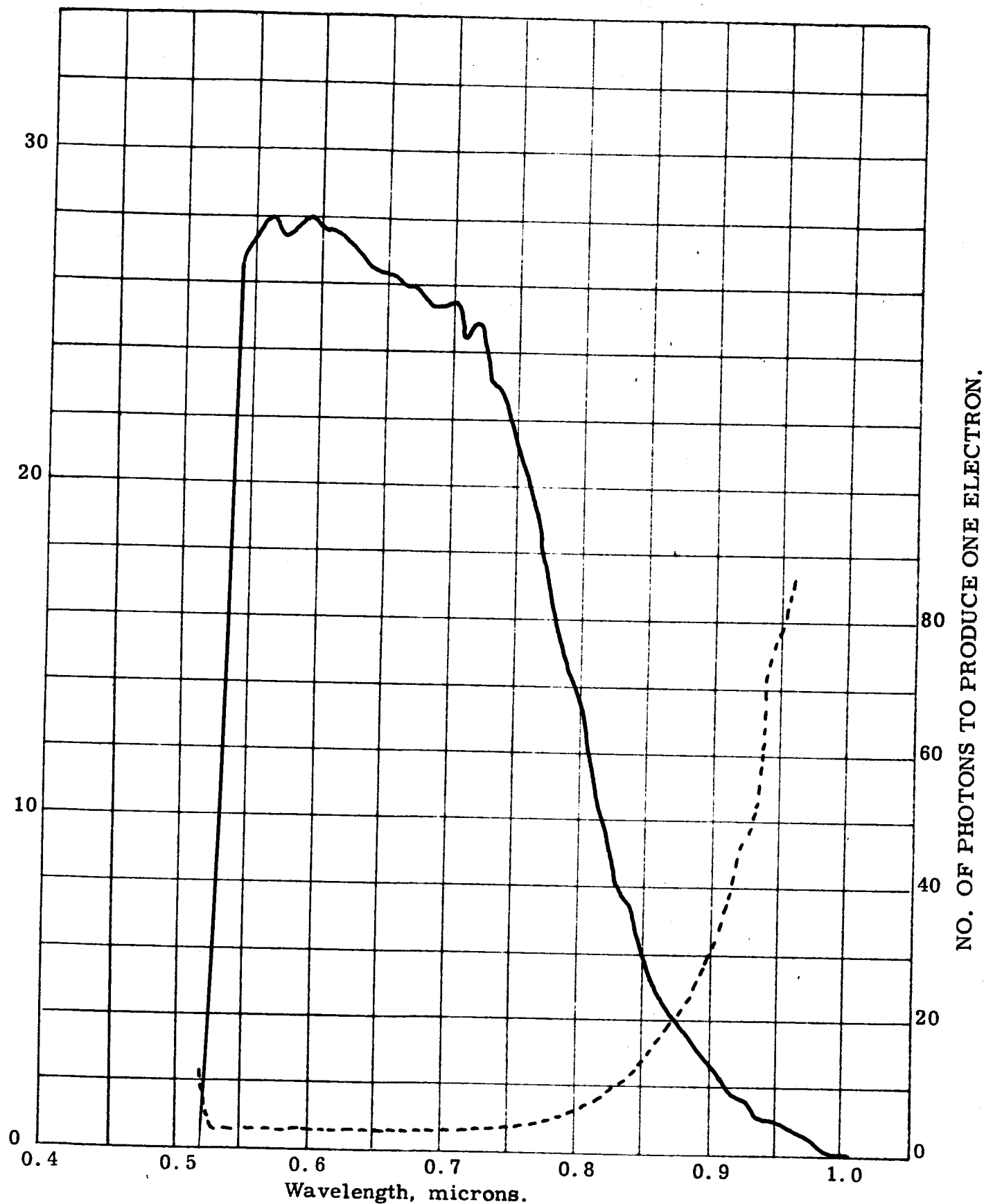
20

Figure 4-6. Spectral Response of CdS Crystal Cell 31T-5-7 for Constant Number of Photons Incident per Unit Area per Unit Time. Number of Photons Incident = 5.23×10^{14} photons-cm^{-2}-sec^{-1}. Solid Curve Is Spectral Response. Dashed Curve Is Number of Photons Required to Produce One Electron.

Typical transmission curves are shown in Fig. 4-7. The upper curve is the percent transmission relative to air of disc T6-1-2, the middle curve is that of disc T6-1-8, and the lower curve is that of disc T6-2-7. It was pointed out in the discussion of Table 4-2 that disc T6-1-2 was a light colored sample and disc T6-1-8 a dark sample from the same bar. Disc T6-2-7 was a dark sample from the second bar. The respective carrier concentrations, and presumably, indium concentrations, are 5.11×10^{17} cm^{-3}, 1.3×10^{18} cm^{-3} and 1.16×10^{19} cm^{-3}, respectively. Discs T6-1-2 and T6-1-8 have the same thickness, approximately 0.10 cm, while disc T6-2-7 is 0.18 cm thick.

It is obvious from Fig. 4-7 that the indium doping concentration (as indicated by the carrier concentration) drastically changes the optical properties of CdS crystals. The estimated indium concentrations for the three samples are 0.0025, 0.005 and 0.05 mol percent respectively for discs T6-1-2, T6-1-8 and T6-2-7.

It was pointed out in the Third Monthly Status Report[4] that the absolute accuracy achieved in efficiency measurements was probably no better than $\pm$ 20%, because it was not known how closely the tungsten photoflood lamp and water filter approximated solar radiation. With the advent of summer and occasionally sunny skies, outdoor efficiency measurements have at last been possible. One of the single crystal cells was measured in both artifical light and natural sunlight. Indoors, and with the solar simulator set at 100 mW-cm^{-2} of radiation the efficiency of the cell was found to be 6.4 percent. Outdoors, in natural sunlight of 80 mW-cm^{-2}, the efficiency was found to be 4.4 percent. Thus, an indicated correction factor of 0.69 should be applied to all previously reported efficiencies. Even this factor is based on very few data, and further measurements will be made, as weather permits, in order to establish a more reliable correction factor. For the future, the artificial light source will be adjusted to equivalent sunlight by varying its intensity to produce a short circuit current exactly equal to that obtained in natural sunlight for a given CdS cell. Alternatively, a silicon solar cell may be used. Since both CdS and silicon cells apparently change with time, this type of measurement will have to be repeated frequently.

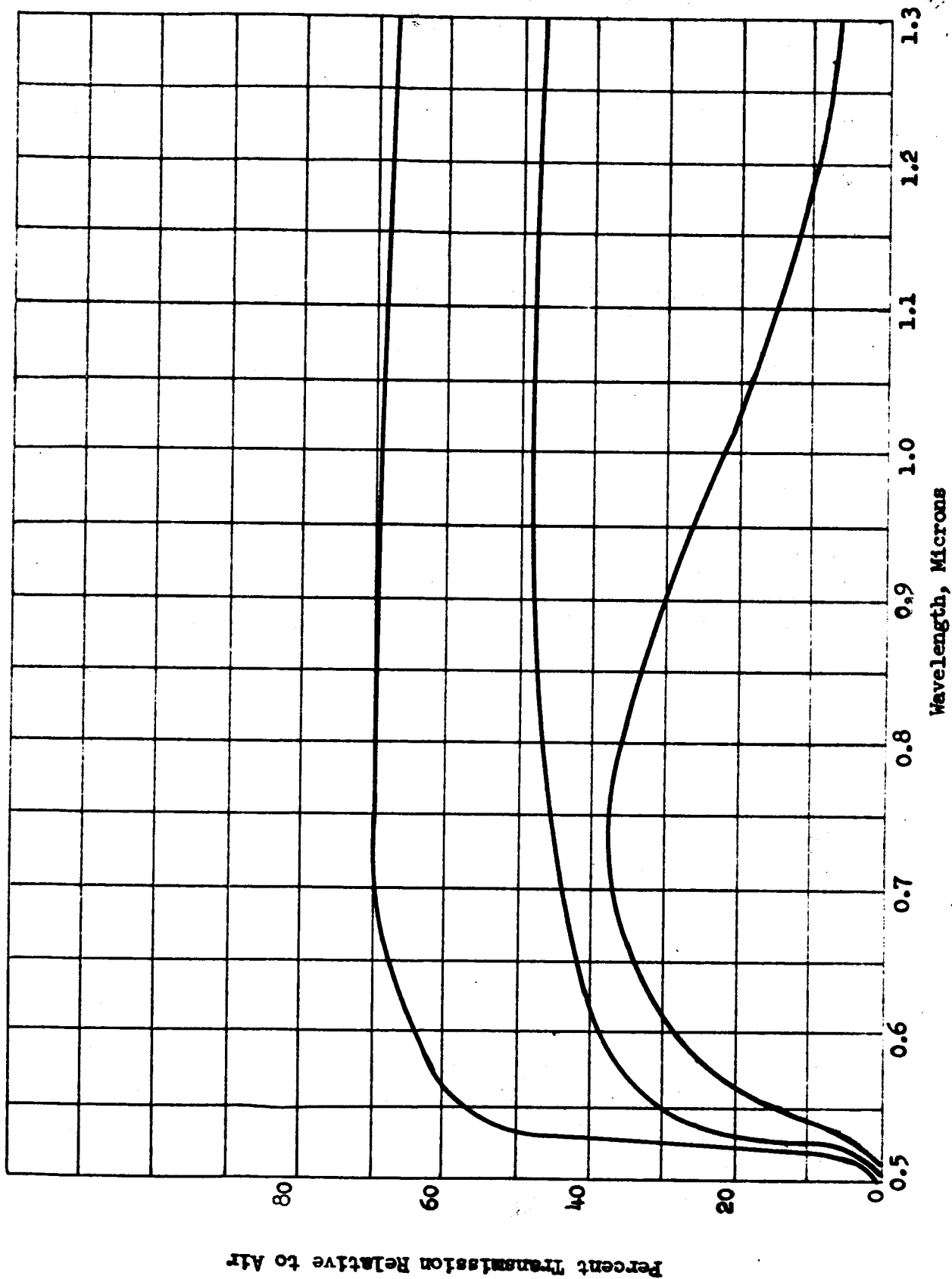CLEVITE CORPORATION   ELECTRONIC RESEARCH DIVISION

Figure 4-7. Spectral Transmission of CdS Crystals Relative to Air.
Upper Curve: CdS Crystal Disc T6-1-2.
Middle Curve: CdS Crystal Disc T6-1-8.
Lower Curve: CdS Crystal Disc T6-2-7.

5. FILM STRUCTURE STUDIES

5.1 X-Ray Studies

In the Second Quarterly Report,[1] it was indicated that the distribution of crystallite particle orientation in films could be best determined with the aid of a pole-figure attachment for the diffractometer. This was designed, and fabrication was completed at the end of this quarter. The device allows the measurement of a given Bragg reflection intensity as a continuous function of sample orientation. Geometric correction of the resultant curves will be accomplished by a normalization obtained from a powder sample of random particle orientation. The principle of operation is most similar to that described by Field and Merchant[5].

Most of the experimental x-ray measurements during the quarter were devoted to determination of average particle size in CdS films.

As standards, samples of General Electric 118-8-2 Luminescent Grade CdS were given successive heat treatments in vacuo; after each, both a Debye-Scherrer film and a diffractometer chart were made. The films were analyzed by Guinier's treatment[6], while diffractometer strip chart reflections were treated by the method described by Klug and Alexander[7].

The Guinier analysis is very qualitative; evaporated CdS films can only be said to contain particles less than one to 10 microns in size. When successive heat treatment of reagent powders produced Debye-Scherrer films of increasing spottiness of the diffraction lines, further heat treatment was pursued; when no further coarsening was noted, even in the lines of the highest back-reflection angles, the powders were deemed to be well over a micron in average size [8].

For diffractometer line broadening analysis, a standard powder sample is needed to establish the minimum instrumental line width for a given crystal and given Bragg reflections. In general, for this purpose, the standard powder must have an average particle size over 1000 to 10,000 angstroms (0.1 to 1.0 micron). This ultimate in coarsening of the CdS powder was achieved after a series of treatments that were found to be equivalent in effect to a single annealing at $600^{\circ}C$ for 4 days. For example, it was found that

2 1/2 hours at 800°C yielded powder of slightly but significantly greater line width.

For these studies, the (002) reflection was most used, due to the strong (002) orientation of most evaporated CdS films with respect to the glass substrates. Reasonable checks were obtained with the (100) and (101) lines, although in the case of "painted" or "sprayed" films apparent anomalies occur; this is interpreted as being due to inconstancy of the "shape factor", K, for different reflections in the well-known Scherrer equation,

$$D = \frac{K\lambda}{\beta\cos\theta} \; , \tag{1}$$

where D is the mean crystallite size, λ is the x-ray wavelength, θ is the Bragg angle, and β is the half-height line breadth (in degrees of measured 2θ units), corrected for $K\alpha$ doublet separation, geometrical factors, and spectral breadths. These corrections have been derived theoretically and verified experimentally, and are presented in graphic form in the literature. Those shown by Klug and Alexander[7] were used after photographing and enlarging.

The above theory of particle size line broadening assumes that internal strains are not present in the crystallites. If one measures the line broadening from a polycrystalline CdS evaporated film, it is obvious that this condition will most likely not be met. Point defects, micrograin boundaries, and dislocations all induce localized lattice strains. At the same time, it could be argued that the line broadening due to unstrained but small powder particles is due to the angstroms-deep, near-surface region of every crystallite, that must necessarily be under new constraints imposed by the surface. As a consequence, it is believed that measurement of "particle size" in CdS films can have a value in assessing structural perfection and in correlating structure-sensitive properties.

Table 5-1 contains those results considered to be meaningful. In many cases, several repetitions were made of a line tracing from a given area on a film sample. It was found that the reproducibility in terms of final calculated "particle size" was well within a spread of ± 10% for ranges of appreciable

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TABLE 5-1. CRYSTALLITE SIZE DETERMINED FROM X-RAY DATA

Specimen Number	Description	D(angstroms)
G.E.118-8-2	CdS powder, Reagent Grade (as received)	21.8 to 23.7
G.E.118-8-2	Heated in vacuo 2-1/2 hrs at 800°C	~ 400
--	Very thin CdS film on glass	12.1
16-3-H	CdS evap. film, etched slightly in HCl	14.7 and 17.6
16-3-I	CdS evap. film, etched as for 16-3-H, and photo-photovoltaic barrier layer applied in usual manner	23.6 and 25.2
16-3-C	CdS evap. film, adherent area	15.6 and 19.0
16-3-C	Area of poor adherence	11.1
18-2-D		22.4
18-3-D	End of film directly over evaporator crucible	17.0
18-3-D	Opposite end, evaporating direction at about 75° to surface	14.7
19-1		11.3
21-3-F		10.5 and 11.1
23-3-R		41.2
24-2		6.7
31-2-B		11.2
31-2-C		11.8
31-2-E	Heated, time and temp. as for barrier formation	14.8
30-1-F	End (a)	13.9
30-1-F	End (b)	19.8
30-1-F	End (a), after annealing 6 hrs at 400°C in Argon	15.8
30-1-F	End (b), after annealing 6 hrs at 400°C in Argon	26.0
32-A-A		9.7 and 11.2
--	Hot sprayed	81.8
K I	Thin slurry, CdS + CdCl$_2$, 600°C, 10 min.	~100 - 400
K II	Thick paste, CdS + CdCl$_2$, 600°C, 10 min.	~400 - 900
--	Flake of black CdS from many successive belljar evaporations	6.4

broadening. At the same time, it was found that the measured line broadening could vary by more than this over a single 1 in. x 2 in. evaporated film sample. These are so noted.

The results in the table include some exploratory experiments. The short heating used in forming the photovoltaic barrier layer always induces a minor amount of particle coarsening; at the same time the much more severe treatment of sample 30-1-F had only about the same effect. The films produced by spraying or slurrying have particle sizes virtually as large as the standard.

Not shown in the table are some anomalous diffraction lines (always (002) and (101)); these are either narrower than the standard or very attenuated in intensity. The reason for this is not yet clear, although the relative weakness of the (002) reflections in those films could be explained by the hypothesis that only a few crystallites happened to be in reflecting position.

There is yet only the most tentative correlation of line broadening with photovoltaic efficiency. Runs 21 and 24 gave reasonably good cells, and both have "particle sizes" at the lower end of the scale. If verified by further experiments, it would be an unexpected result, inasmuch as one would intuitively expect a film of least disorder to be more like a single crystal in yielding higher efficiencies.

5.2 Electron Microscopy

The technique used was a standard one, involving replication by Formvar and collodion, followed by shadowing with palladium and backing with evaporated carbon. In the following photographs, the clear distance between the bar shadows is approximately one micron.

Figure 5-1 shows a feature found on a sample of as-received-from-the-supplier glass used for thin film substrates. Another sample was cleaned in the usual manner (detergents, degreasers, acids, and water). Figure 5-2 is fairly typical of a wide variety of hexagonal features found varying in maximum dimension from less than 1 to over 15 microns. Figure 5-3 is typical of many
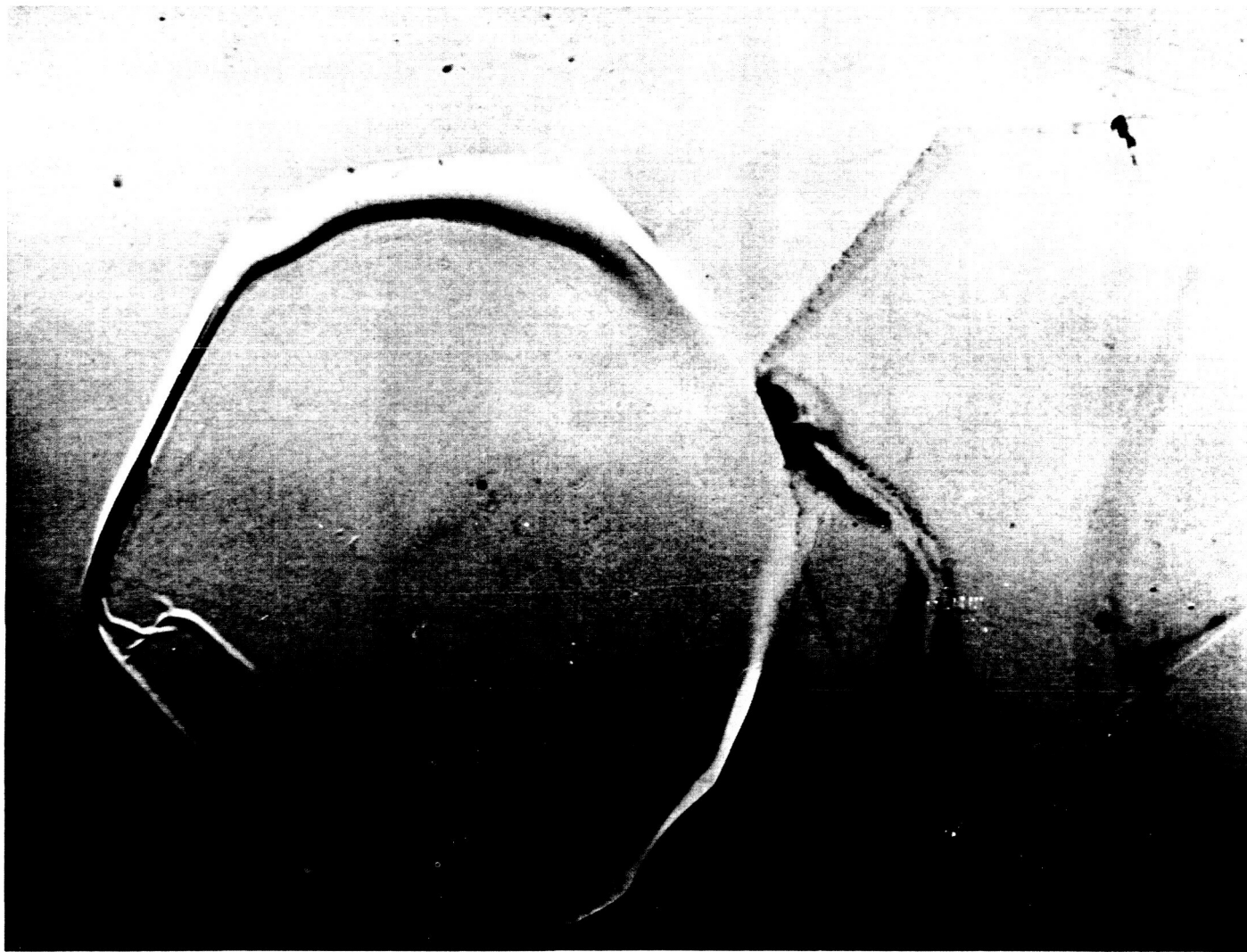
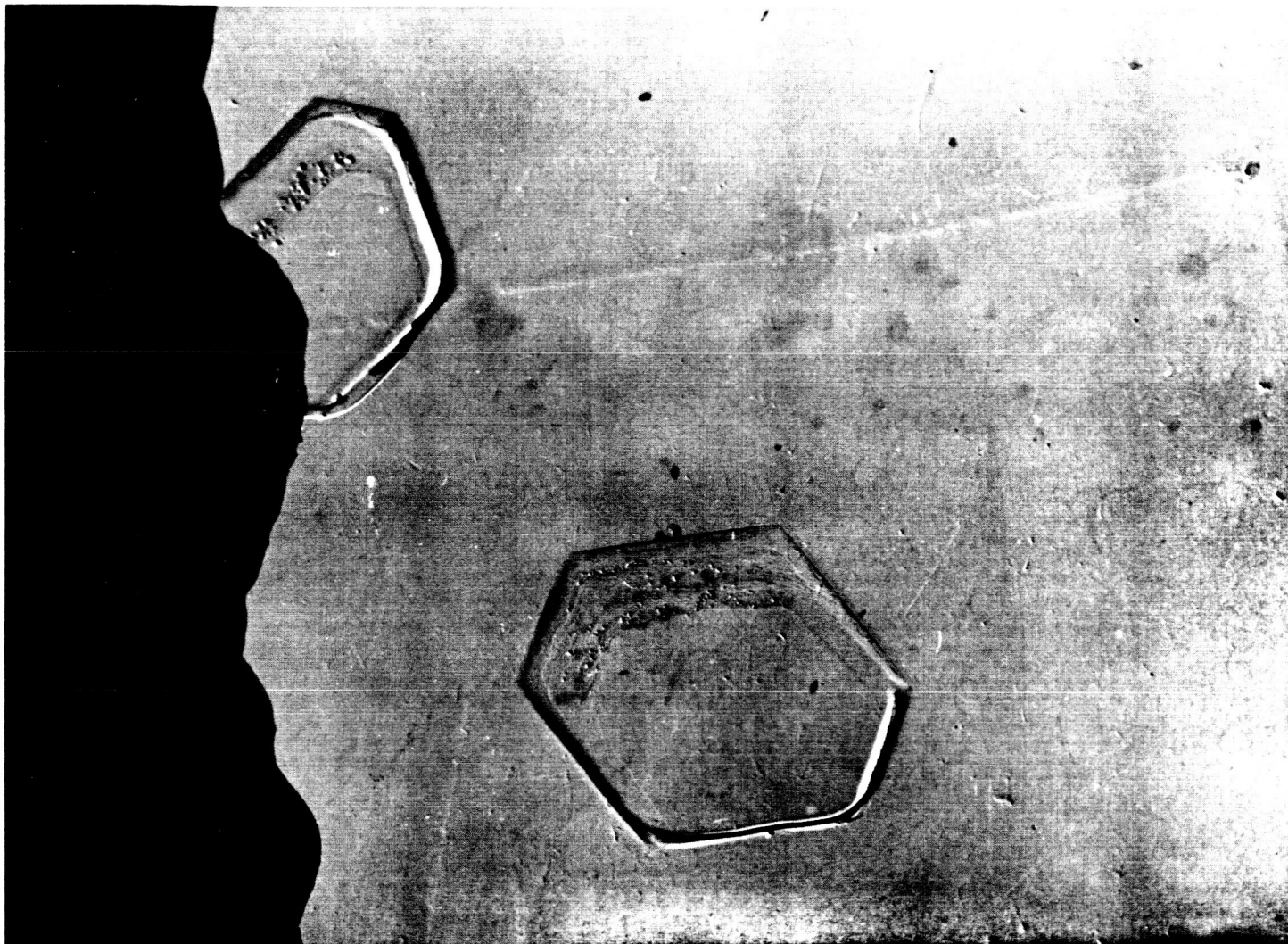Fig. 5-1. Glass used for CdS evaporation substrates; Sample I.

Fig. 5-2. Glass used for CdS evaporation substrates; Sample II.
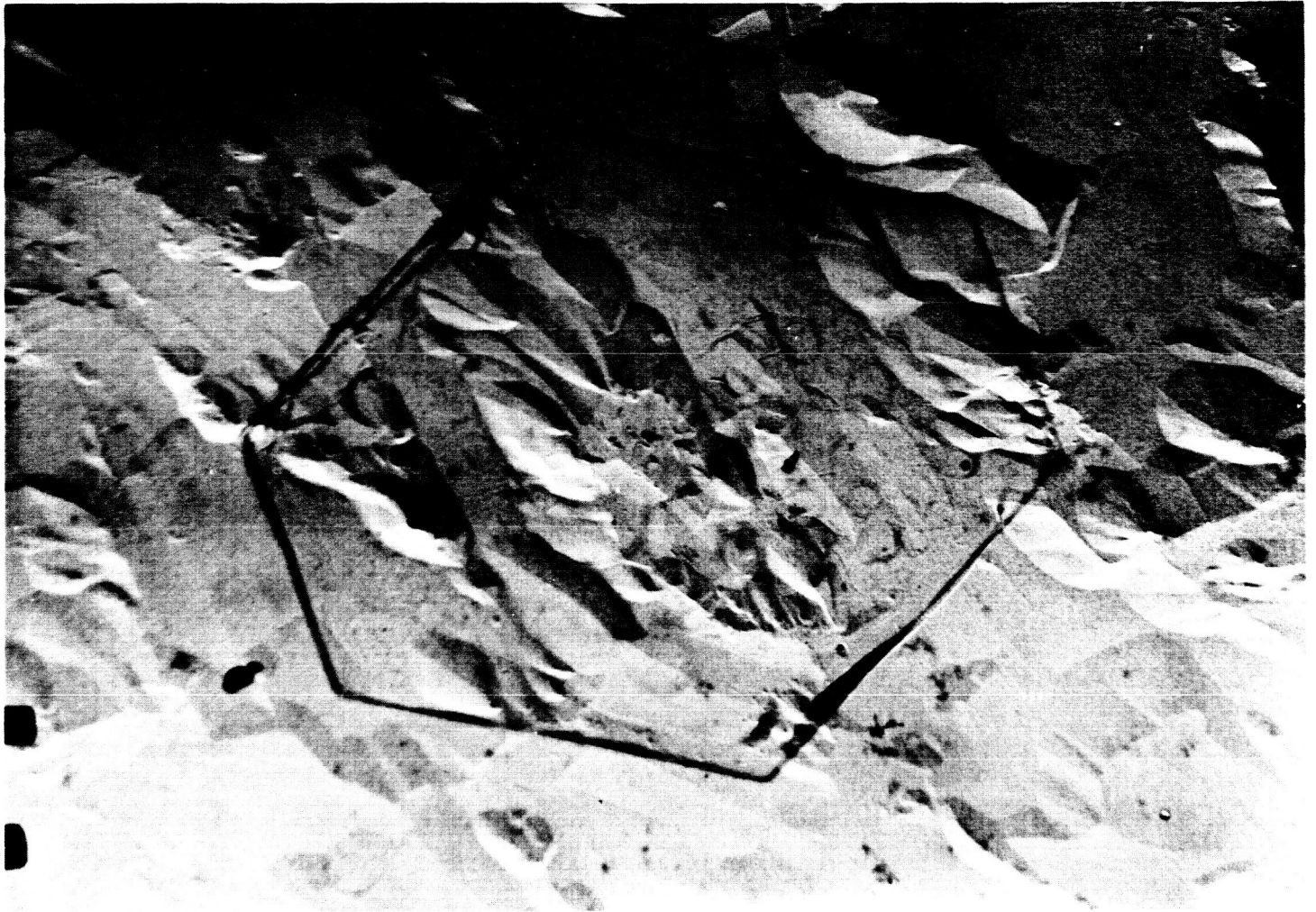
Fig. 5-3.   CdS evaporated film 21-3-F.

such features found in film 21-3-F. Figure 5-4 is a stereo pair of the same area. The overall surface of 21-3-F was found to be relatively smooth, with features that appear to be hillocks until carefully viewed stereoscopically; in Fig. 5-4, at least, they are undoubtedly pits. The hexagonal feature here is sharply defined, but without relief, the outline being ~ 1/10 micron wide. Inasmuch as several dozen photographs of both glass and film surfaces indicate the hexagonal figures to be derived from the glass, it is indeed astonishing that they remain so sharply defined after deposition of about 25 microns of polycrystalline CdS (21-3-E was measured to be 28 microns thick).

Figure 5-5 is a portion of CdS film 16-3-C, showing another variation of the hexagonal figure, together with some of the smaller nodule-like depressions (or hillocks) found in great numbers on micrographs of this film. Figure 5-6 is of another 1 in. x 2 in. film from this run, 16-3-H, after etching with HCl. The many closely-spaced etch pits suggest the imperfection density to be far higher than might be supposed from the rather planar crystal-like facets on the surface of 16-3-C (Fig. 5-5).

CdS film 16-3-I was acid-etched exactly as 16-3-H, but was then given a copper barrier layer by the currently standard procedure. Figure 5-7 shows the result. There has been an apparent increase in the density of etch pits, and the ridges that rise above the general plain are lower.

Figure 5-8 shows the typically rough surface found in 18-3-D, together with a hexagonal figure. Figure 5-9 is a stereo pair from 18-3-D that discloses the surface to be composed of a system of reasonably flat-topped ridges separated by sharply incised crevices.

Figure 5-10 is an electron micrograph of a sprayed CdS film. The film structure is not as cohesive as in the evaporated films, and tearouts occur in replication. These are the black, globular areas in Fig. 5-10, and in most areas of the replica were much more serious.

Just as for the data on "particle size" in films, the electron micrographs thus far fail to provide any clear correlations of film topography with photovoltaic efficiency. Neither the source of the hexagonal figures on the glass nor their effect on the semiconducting properties of the CdS films is known. While it presently seems unlikely from available evidence, it may yet be discovered that the hexagonal figures arise in some manner in the replication process.

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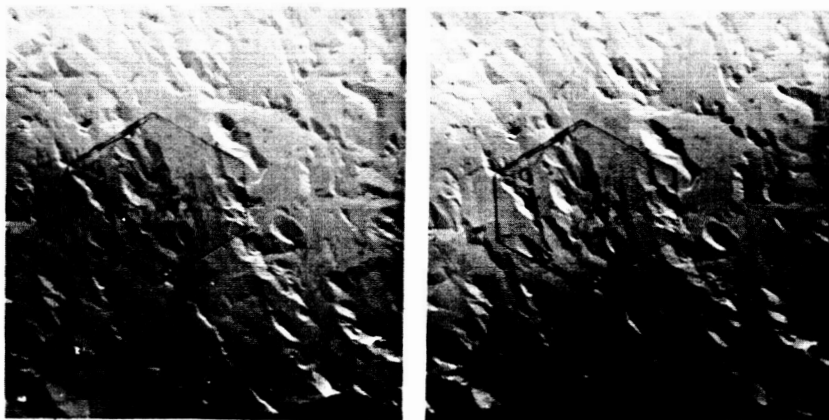
Fig. 5-4. Stereo pair of area of CdS film 21-3-F shown in Fig. 5-3.
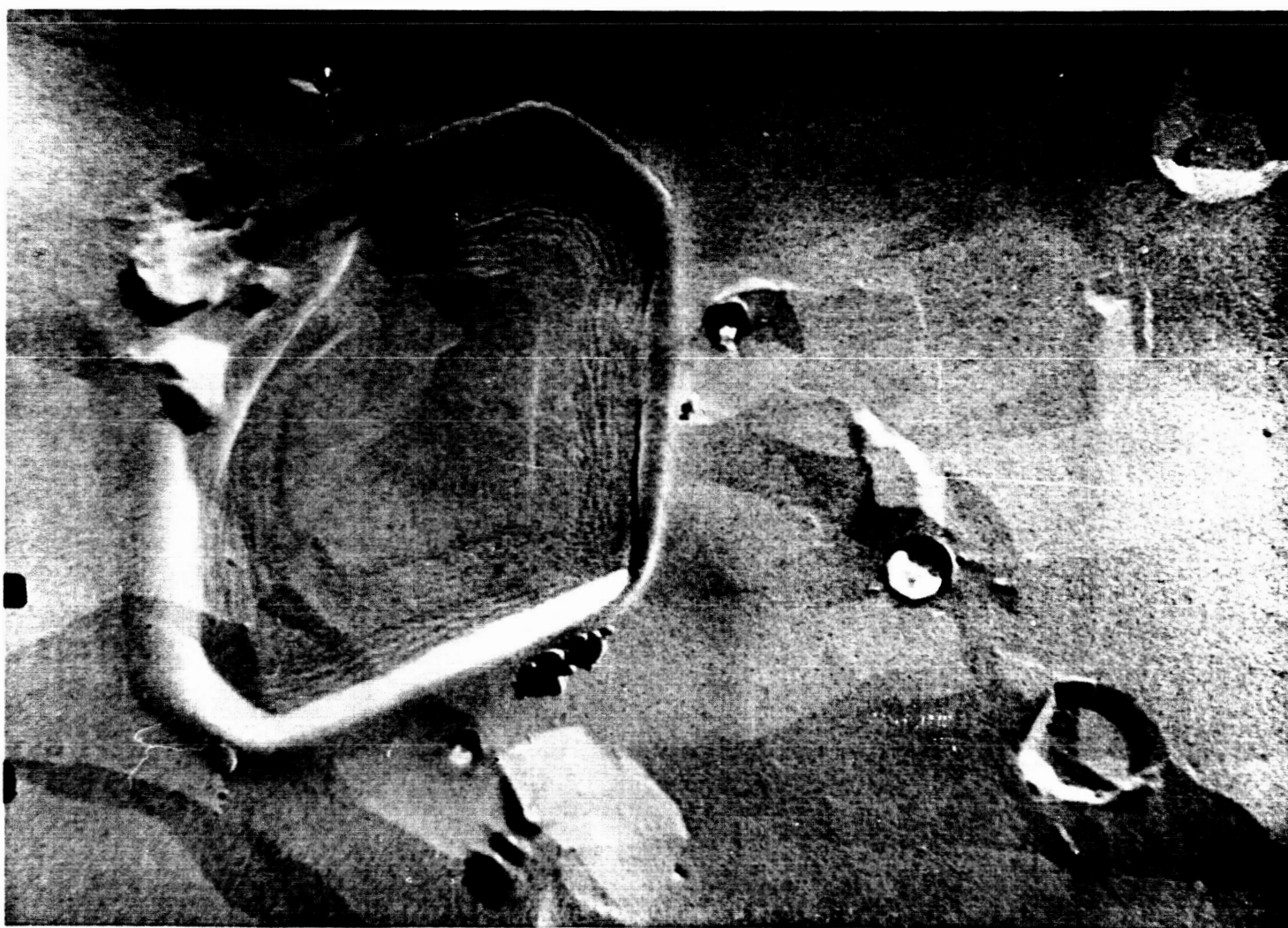
Fig. 5-5. CdS evaporated film 16-3-C, untreated.
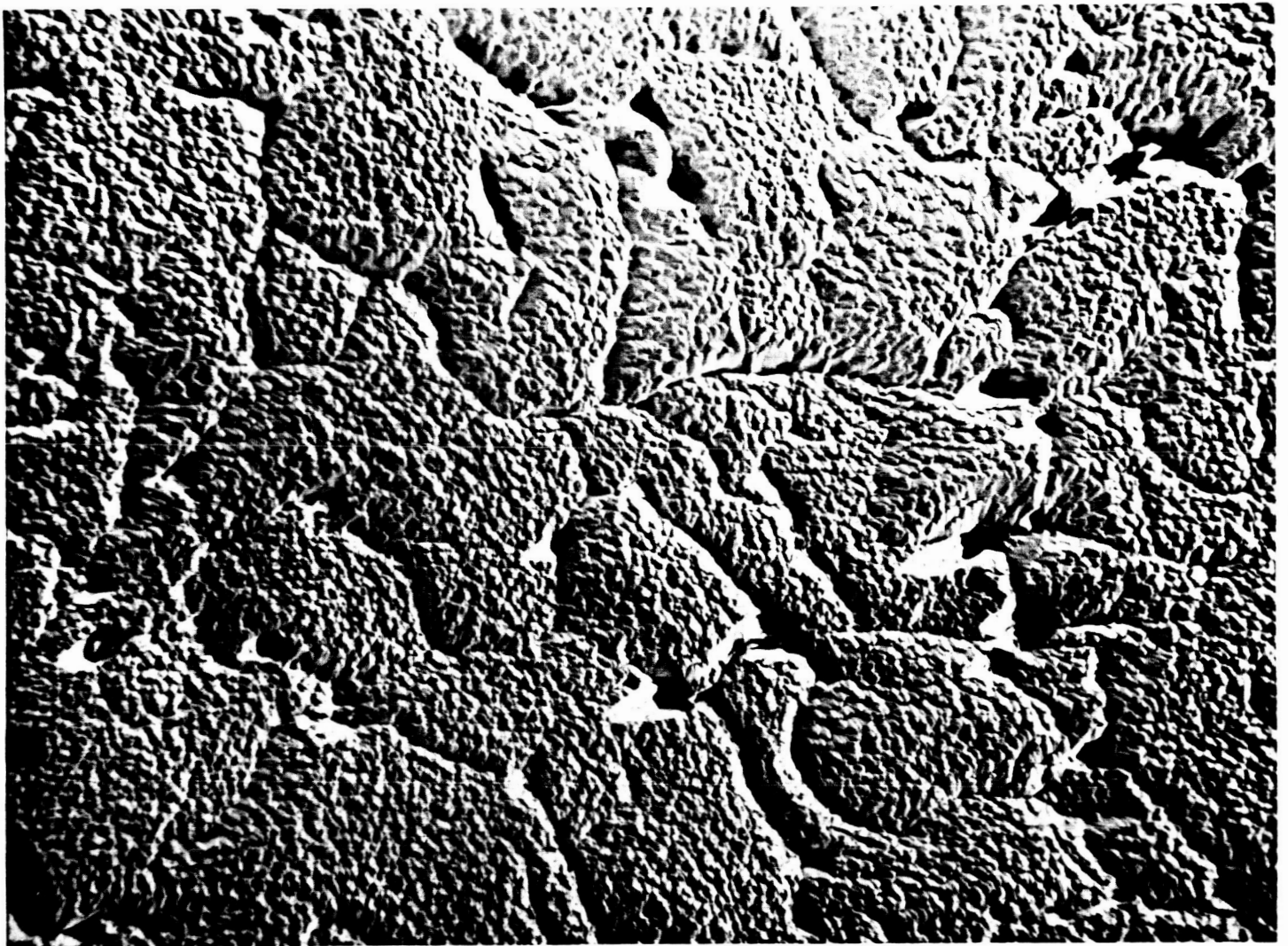
Fig. 5-6. CdS evaporated film 16-3-H, etched in 1:1 HCl, 5 seconds.
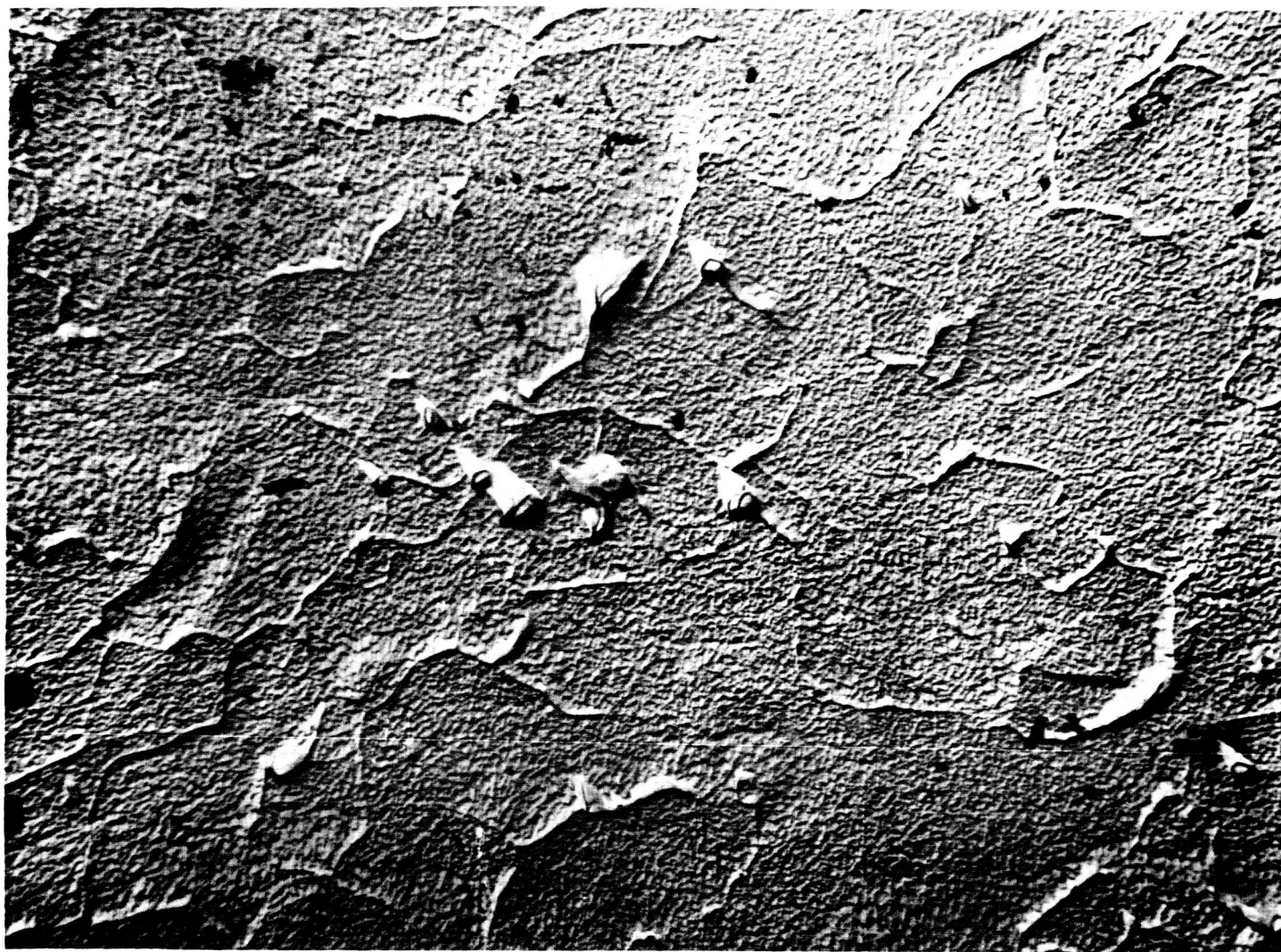
Fig. 5-7. CdS evaporated film 16-3-I, etched in 1:1 HCl, 5 seconds, followed by formation of copper photovoltaic barrier layer.
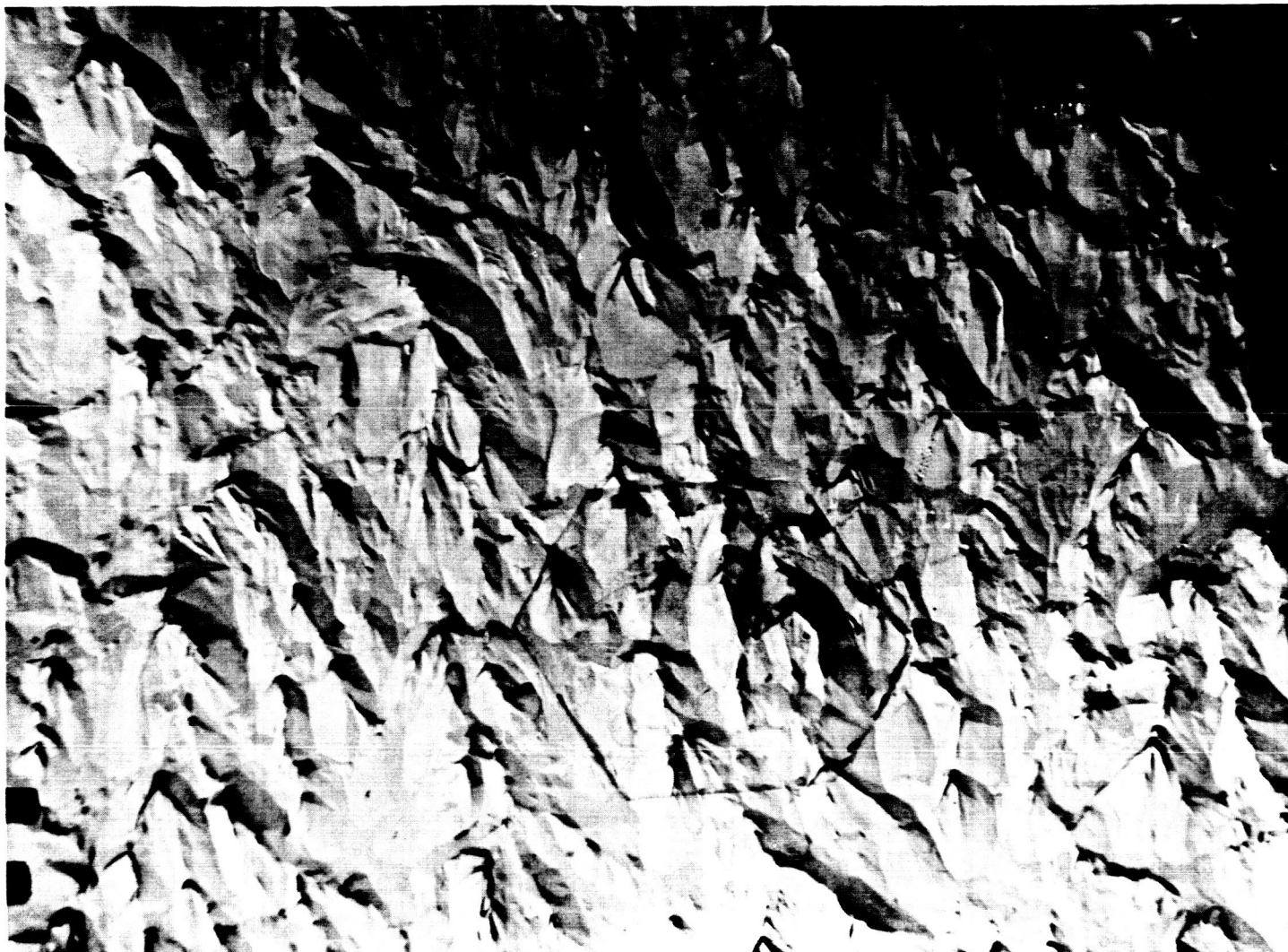
Fig. 5-8. CdS evaporated film 18-3-D.
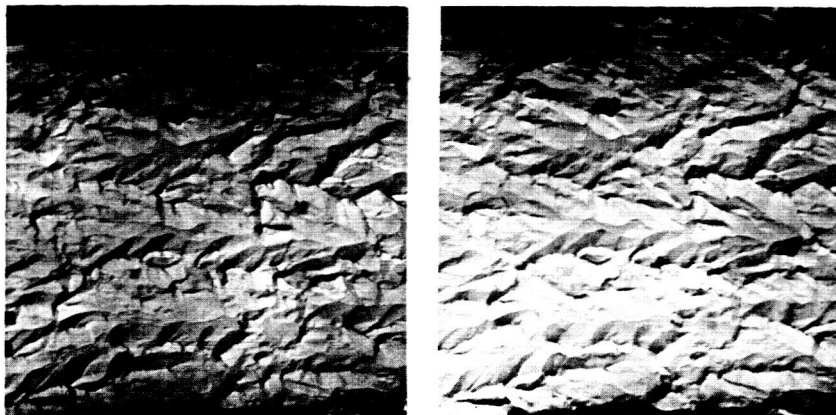
Fig. 5-9.   Stereo pair of CdS film 18-3-D.

Fig. 5-10.   CdS film formed by spraying $CdCl_2$ + H_2S on hot glass.

6. ALTERNATE METHODS OF PRODUCING CdS FILMS

The "wet chemistry" approach to producing CdS films was started
in December of 1962. The work was performed by Mr. M. P. Makowski under the
direction of Dr. M. L. Selker of the Mechanical Research Division of Clevite
Corporation. A summary of Mr. Makowski's work is given in the Appendix to
this report.

Since April, 1963, the work has been carried out in the Electronic
Research Division by Mr. John Koenig.

6.1 Sintered Films

A number of experiments based on a United States Patent issued to
S. M. Thomsen[9] were carried out in an attempt to produce adherent, indium-
doped cadmium sulfide films on glass substrates. An essential feature of this
technique is the use of $CdCl_2$ as a flux which dissolves CdS and evaporates at
approximately $600^\circ C$, leaving a firmly adhering layer of interlaced CdS crystal-
lites. The film samples were sintered in a 1.125-inch diameter, 14-inch long,
quartz muffle housed in a specially built furnace. The subliming $CdCl_2$ con-
densed in the cold neck of the quartz tube which extended about six inches out-
side the furnace. The substrates were the same as those used in vacuum evapor-
ation: pyrex plates 1 in. x 2 in. x 1/8 in., cleaned as for evaporation and
flamed just before use.

6.2 Materials

The starting materials employed were General Electric Co. Luminescent
Grade CdS powder, indium-doped CdS crystals grown in this laboratory, indium
chloride obtained by dissolving the pure (99.97%) metal in hydrochloric acid,
high purity commercial indium sulfide crystals and cadmium chloride crystals.

6.3 Discussion of Experiments

Two substrates were coated with a slurry made from indium-doped cad-
mium sulfide crystals and 12.5 wt percent cadmium chloride. The crystals were
breakage from boule T-7 and nominally doped with 0.05 mol percent indium sul-
fide. The mixture was ground in a hand mortar with a small amount of water
added to produce a heavy slurry. This was brushed on a substrate. The slurry
was thinned with more water and brushed onto another substrate. Both substrates

were dried at 105°C and sintered at 600°C for ten minutes in an argon atmosphere. The thick slurry yielded a thick, orange-yellow layer. Its adherence was good and no pinholes or cracks were observed. The layer was uneven and exhibited reddish areas. The resistance was high: 10^5 to 10^6 ohms between indium probes 5 mm apart. The light slurry produced a thinner CdS layer similar to the thick layer in appearance except that many pinholes were observed. Surprisingly, its resistance was considerably less: 10^3 to 10^4 ohms between indium tipped electrodes 5 mm apart.

Another slurry was prepared using CdS powder, 12.5 wt percent cadmium chloride (in solution) and 0.1 mol percent indium chloride (in solution). Water was added to produce a thin slurry which was brushed on several pyrex substrates. The films blistered during drying. After sintering in argon at 600°C for ten minutes, the films cracked and flaked off the substrate.

In another experiment, CdS powder, cadmium chloride and 0.05 mol percent finely ground indium sulfide were mixed with water and ball milled for several hours in a plastic jar with burundum stones. A moderately heavy slurry was obtained and applied to pyrex plates by screening or by rolling on with a 1/4-inch diameter pin. Some of the slurry was thinned with water and sprayed onto a substrate. After drying at 105°C, sintering was carried out in several ways. It was expected that the indium sulfide would form a solid solution with the CdS. The screened film was sintered for 5 minutes in air at 600°C. The layer was well adherent, uneven in thickness and was yellow with reddish areas. The resistance was 10^6 ohms with probes 5 mm apart. One rolled film was sintered for 90 minutes in argon at 550°C. Adherence was good, but again the thickness was uneven and contained many short cracks. Resistance ranged from 10^4 to 10^6 ohms. The other rolled film was sintered over the open flame of a Fisher burner. This film adhered exceptionally well, and in isolated areas had resistances as low as 400 ohms between probes. The sprayed film, sintered for 30 minutes in argon at 600°C, exhibited very poor adherence.

In general, these experiments confirm the results of the sintered CdS-InCl$_2$ experiments discussed in the Appendix. This effort is now being directed toward the deposition of CdS on flexible substrates at low (<300°C) temperatures.

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7. APPENDIX

DEPOSITION OF CADMIUM SULFIDE FILMS BY CHEMICAL METHODS
M. P. Makowski, Mechanical Research Division
Clevite Corporation

INTRODUCTION

The work described herein was initiated on December 1, 1962, by request

of the Electronic Research Division of Clevite Corporation and carried through

March 1963.

The objective of this study was to explore "chemical" methods of deposition

of cadmium sulfide films on various substrates for the purpose of obtaining a

suitable photovoltaic cell material. It was felt that our experience in various

film and plate forming processes might lead to a development of a suitable photo-

voltaic film either by a direct application of our knowledge in the field or by

developing other techniques.

It became apparent at the outset that it would be of great value to develop

a process involving deposition from solution similar to an electroless process

for metals. Accordingly, about half the alloted time was spent on this approach.

Spray techniques were investigated next, followed by sintering techniques and

various combinations of the earlier methods.

The exploratory nature of this short study required that general "probing"

for profitable modes of attack should be undertaken, even, in some cases, at

the expense of detail and thoroughness. The work was planned with these guide-

lines in mind and to insure the widest possible coverage of the field.

SOLUTION METHODS

A. Alkaline Thiourea System without Complexing Agents

The desired chemical process of formation of cadmium sulfide film from solution might be represented by the overall equation:

$$Cd^{++} + 3OH^- \longrightarrow HCdO_2^- + H_2O \qquad (A-1)$$

$$HCdO_2^- + \underset{NH_2}{\overset{NH_2}{C}} = S \longrightarrow CdS + H_2NCN + OH^- + H_2O \qquad (A-2)$$
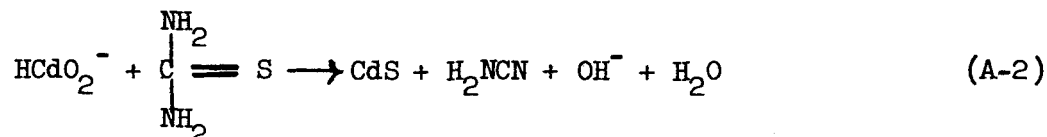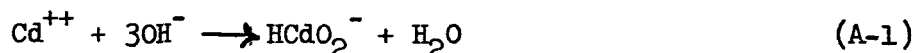
Equations (A-1) and (A-2) are written by analogy to a known process for deposition of lead sulfide films (mirrors)[10,11] and are used here only to portray the scheme and not to imply any mechanism by which such a scheme might be carried out. Actually, it was quickly established that a mere substitution of cadmium for lead in a formulation according to the process represented by equations (A-1) and (A-2) was not possible, that is, no films of CdS were obtained. Instead, voluminous precipitate formed quickly within the bulk of solution whenever solutions of cadmium salts, thiourea and sodium hydroxide were brought together at room temperature. The reaction proceeded through a formation of white precipitate which soon turned yellow. This part of the reaction is analogous to the lead sulfide reaction in which a white precipitate forms in addition to film formation on a substrate. The white precipitate then changes color to black.

The work was carried out in 150 ml beakers, using measured amounts of solution, which, after mixing with water in the order indicated had the following approximate composition:

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0.006 mole/ l $Cd(NO_3)_2$ or $Cd(CH_3COO)_2$

0.03 " Thiourea

0.006 " NaOH

Pyrex glass substrates were cleaned by degreasing, scouring with detergent powder, rinsing, 2 min. immersion in 20% NaOH at 80-85°C, and rinsing in deionized water. This, or similar treatment was followed with many samples, and even if not mentioned, such treatment is always implied.

The fact that the precipitate formed quickly showed that it was necessary to find means by which the reaction could be controlled and directed to the surfaces of the substrate, as was the case in the lead system. The sulfur necessary for the formation of cadmium sulfide was already bound in thiourea from which it was released relatively slowly, as indicated by the fact that a white precipitate appeared first which only later changed into yellow. Thus, it was thought that cadmium must be also bound into a complex from which it could be released as required, as by heating of the solution. A search for complexing agents suitable for the purpose yielded a list of likely compounds listed in Table A-1. Only one of these reagents (EDTA) was actually used, but the list may be found useful at a later date, should a further study of this system be made. The figures in Table A-1, listed under $\log K_1$, represent the logarithm of the complex stability constants (equilibrium constants for complex formation),[12] in accordance with the equations

$$CdL_{n-1} + L = CdL_n, \tag{A-3}$$
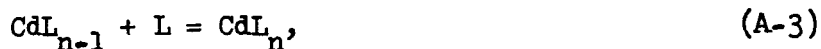
$$K_n = \frac{(CdL_n)}{(CdL_{n-1})(L)} . \tag{A-4}$$

where L = ligand.

TABLE A-1. SELECTED COMPLEXING AGENTS FOR CADMIUM

No.	Ligand	Log of Stability Constants log K_1
1.	Dimethylglyoxime	5.7
2.	Ethylenediamine	5.8
3.	1:10 - phenanthroline	6.4
4.	Methyliminodiacetic acid	6.77
5.	N-(carbamoylmethyl)imino-diacetic acid	7.08
6.	8-hydroxyquinoline	7.2
7.	N-2-hydroxyethylimino-diacetic acid	7.52
8.	2-methoxyethyliminodiacetic acid	7.53
9.	8-hydroxyquinoline-5-sulphonic acid	7.6
10.	Benzoylacetone	7.79
11.	2-methylthioethyliminodiacetic acid	7.89
12.	2:2'-diaminodiethylamine	8.45
13.	Benzoyl-2-furoylmethane	8.46
14.	Dibenzoylmethane	8.67
15.	Nitrilotriacetic acid	9.0
16.	8-hydroxy-2-methylquinoline	9.0
17.	NN'-Di-(2-aminoethyl) ethylenediamine	10.8
18.	Ethylenediamine-NN-diacetic acid	10.58
19.	2-mercaptoethylamine	10.97
20.	1-0-hydroxyphenylazo-2-baphthol	13.03
21.	Trimethylenediamine-NNN'N'-tetraacetic acid	13.45
22.	1-(5-chloro-2-hydroyxphenylazo)-2-naphthol	13.46
23.	2:2'-bis (di(carboymethyl)amino)diethyl sulphide	14.0
24.	Ethylenediaminetetraacetic Acid (EDTA)	16.5
25.	2-mercaptoethyliminodiacetic acid	16.72
26.	NNN'N'-tetrakis-(2-aminoethyl)-ethylenediamine	16.80
27.	2:2'-bis(di(carboyxmethyl)amino)diethyl ether	17.75
28.	1:2-diaminocyclohexane NNN'N'tetraacetic acid	19.23

B. Alkaline Thiourea Systems with EDTA as a Complexing Agent

Tetra-sodium salt of ethylenediaminetetraacetic acid (EDTA) was the only complexing agent tried for reasons of high complexing power and ready availability. It is also representative of a group of high-power complexing agents, as is evident from Table A-1.

In order to insure full complexing of cadmium ion, an excess of EDTA was added, 0.012 mole/l, to the formulation described on page 44. With this modification it was possible to keep the solution for 24 hours without any visible decomposition. It was found later that the amount of EDTA could be reduced to about 0.005 mole/liter if the amount of NaOH was kept down to a level corresponding to pH = 10.5. This reduction of the amount of EDTA was found to be necessary to start the CdS-forming reaction at temperatures about 80-90°C. A number of deposits were prepared on glass (Pyrex) but they were all thin, powdery, and nonadherent.

It was noted at this stage that one of the difficulties in this approach was the quick coagulation of CdS and settling down to the bottom of the beaker once the CdS forming reaction was started by heating. There was, consequently, very little time available for the small CdS crystals, which were just formed, to attach themselves to the substrate before they encountered other crystals and formed an agglomerate. It appeared that this problem could be minimized by providing some reagents to keep the freshly formed precipitate in suspension long enough to have a chance to deposit on the substrate in a dense, adherent layer. After some experimentation, it was found that small amounts of polyvinyl alcohol added to the solution helped to produce better deposits. Polyvinyl alcohol is mentioned in the literature on lead sulfide[10] in connection with the "seeding solutions" which

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are used on substrates prior to application of the main solution. Once the beneficial effect of polyvinyl alcohol had been established, all subsequent samples were processed through the seeding solution consisting of:

225 ml water,

10 ml o.35% cadmium nitrate,

5 ml 0.5% polyvinyl alcohol soln,

10 ml 0.2N (saturated) solution of hydrogen sulfide.

This modification of the process represented an improvement, but it did not provide films of CdS comparable in quality with the PbS films obtained from similar formulations.

Doping of the cadmium sulfide film with indium in this process presented an additional difficulty. The solutions were alkaline and an addition of an indium chloride solution (prepared by dissolving indium metal in HCl) in small amounts invariably resulted in an immediate formation of a white precipitate presumably indium hydroxide, which rendered the bath useless. In order to incorporate indium into the system, the electroplaters' technique of using dextrose in highly alkaline solution was followed. In a number of tests, sodium cyanide was added to the solution [13]. A typical level of concentration of indium in the final bath in this series was 0.002 - 0.02 mole/l (equal to or higher than the cadmium concentration); but levels much lower than this were also tried.

The EDTA-polyvinyl alcohol-stabilized and indium-doped baths, described above, were used to deposit cadmium sulfide on various substrates. A brief description of representative results of this "immersion method" follows:

Pyrex glass. Loose, powdery deposits were obtained. Adhesion was poor. Practically no electric conductivity could be tetected.

Microscope slide glass. Results were as on Pyrex, except that there was some adhesion noted on the frosted portions of the glass.

Glass tape. (Corning capacitor glass, containing up to 10% lead). Some slight deposit was obtained after about 20 mins. heating (about 90°-95°C). Adhesion was poor; however, after removing the loose deposit the specimen retained interference-type coloration and a number of very small dark spots, visible under magnification of about 30X. The nature of the spots is not clear.

Conductive glass. Conducting glass sheet was cut to approximate dimensions of 1" x 4" and treated, as described above. Of all glass samples the conductive glass gave the best results. The CdS films were relatively well-adhering and continuous. The films generally adhered better on the SnO_2-coated side. Actually, only these glass specimens, of all glass samples processed by this immersion method, withstood the "Scotch Tape Test" on the SnO_2-coated side, i.e., cadmium sulfide was not lifted by 1/2" Scotch tape which was pressed (with fingers) onto its surface and peeled off after several seconds. The parameters studied with these substrates were: length of time spent in the seeding solution (from 3 min. to 9 days), length of time spent in the bath (from several minutes to 2 hours), and variations in indium content in the bath. No significant differences were noted on varying these parameters, although a definitely better film was obtained with longer seeding times.

Mica. Very loosely adhering deposits of CdS were obtained on this substrate. In addition to the regular pretreatment of the sample, as described above, the mica samples were sensitized and seeded by a stannous

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chloride-silver nitrate-palladium chloride dip sequence, but this did not relieve the adhesion difficulty.

DuPont H-Film. Serious adhesion problems were encountered with this substrate as well. Several short tests were conducted to check if the surface of DuPont H-film could be conditioned to receive a layer of CdS from solution, as above. It was found that, although the film is attacked by hot 20% NaOH, as indicated by swelling and deterioration of the film on edges, the CdS did not stick to the film. Vapor degreasing in trichloroethylene and soaking for 24 hours in carbon disulfide and dimethylformamide did not contribute to better adhesion. In an effort to provide an intermediate layer on H film, electroless nickel was deposited on the film after the sensitizing treatment described above under mica, employing an electroless nickel bath due to Narcus. An additional step consisting of a short immersion of the specimen in 10% sodium hypophosphite solution just prior to immersion in the nickel bath, was added to insure fast reaction and good coverage. The adhesion of the nickel film was good, but when the specimen was immersed in a cadmium sulfide forming bath, the nickel film became detached before any cadmium sulfide could form on it.

Clevite Copper Foil. A significant portion of time spent on "immersion methods" was devoted to attempts at deposition of cadmium sulfide on the oxidized side (Cu_2O) of copper foil. Samples 1" x 4" in size were used. All samples were cleaned in detergent, etched in HCl for 10 seconds and rinsed with deionized water. Some specimens were seeded, as above, others were not. The compositions of the cadmium sulfide-forming baths were varied, as with the other substrates. As a rule, the adhesion of CdS to the oxidized side of the foil was much better than to the other substrates. Some very weak photovoltaic

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effect was noted on deposits from baths without indium, using a Keithley Electrometer #610A. The effect was more pronounced (about 5 mV) on specimens treated in indium-containing baths.

C. Plating and Sulfiding Methods

Preliminary tests with pieces of cadmium metal immersed in solutions containing sulfur compounds such as thiourea, thioacetamide, etc., produced well-adhering layers of cadmium sulfide on the surface. On the basis of these tests, a series of experiments was designed to check the feasibility of the plating and sulfiding method for deposition of CdS on copper foil because the conductive layer on glass was apparently attacked by the highly alkaline plating baths.

The following electroplating baths or their various combinations were used in these studies[13]:

Cadmium: 30 g/l CdO
                                    100 g/l NaCN
                                    7.5 g/l NaOH

Indium: 20 g/l In (as chloride)
                                    150 g/l NaCN
                                    35 g/l NaOH
                                    35 g/l Dextrose.

At first, a two-layer plating method was tried. Indium was plated for about 20 seconds at 0.4 amp (c.d. about 0.01 amp/cm^2). The samples were rinsed and plated with cadmium for 2 minutes at 0.5 amp (0.012 amp/cm^2), whereupon they were rinsed, dried and heated for 2 minutes in oven at 300°C.

Alloy plating was used in another series of tests. In this group, the molar ratio In:Cd in solution was varied from 1:20 to 1:1 approximately. No

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solubility problems were encountered in mixing the solutions. The current densities and times of plating were comparable to those used in the two-layer plating.

All plated samples were subjected to various solution sulfiding procedures, such as prolonged treating in solutions of thiourea, thioacetamide, ammonium sulfide, and the "balanced" thiourea-EDTA bath described above. Well-adhering layers of cadmium sulfide were obtained in most cases.

The two-layer plating method, including the diffusion heat treatment (2 min. at 300°C) before and a short heating after sulfiding, produced photovoltaic response amounting to several millivolts. It was also found that photovoltaic response of similar magnitude was registered on samples plated with indium, omitting the cadmium plating step, and sulfided in a balanced thiourea-EDTA bath. The alloy-plated samples produced no photovoltaic effect.

One of the difficulties of the sulfiding approach, when copper foil was used, was the formation of copper sulfide, especially on edges of the foil where the plate was probably not continuous. This disturbing side reaction must be controlled in some way, should interest in this method be revived.

D. Other Solution Methods

In order to test the effect of concentration of reagents in solution on the film-forming properties, highly dilute solutions, or more properly, colloidal sols of cadmium sulfide were checked. The seeding solution, containing about 0.001 moles of Cd^{++} and about 0.004 moles of H_2S per liter, was used for this purpose. No visible deposition of CdS took place on immersion of copper foil

in this solution for 24 hours.

Taking a lead from a recent paper by Sato[14], a short test was carried out to check on the possibility of the following reaction on a thin layer of lead sulfide:

$$PbS + Cd^{++} \longrightarrow CdS + Pb^{++} . \tag{A-5}$$

The results were negative when the lead-sulfide layer on Pyrex was exposed to a solution containing cadmium nitrate and thiourea for a prolonged time. The only effect noted was peeling of the lead sulfide from the glass at the solution-air interface.

Another attempt to cause the formation of cadmium sulfide on the surface, and not in the bulk of solution, was carried out by bringing together a solution of sulfur in carbon disulfide with an aqueous solution of cadmium salts. No reaction took place at the interface of the two phases. When a solution of H_2S in carbon disulfide was contacted with an aqueous solution of cadmium salts, the reaction at the interface, and soon thereafter in the bulk of the aqueous phase, was hard to control for the purpose of film formation.

In an effort to modify the surface of the substrate, a series of tests was carried out with glass samples covered with sodium silicate (water glass). The sodium silicate coat was dried prior to insertion into the balanced thiourea - EDTA bath. The results were negative, primarily due to the ready solubility of sodium silicate (even after drying) in the alkaline medium.

SPRAY METHODS

In spite of some degree of success achieved by employing the solution methods, it was obvious that such methods required a considerable amount of additional exploratory work to produce cadmium sulfide deposits which

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might approach the quality of vacuum - deposited samples. Thus, in keeping with the nature of this assignment, attention was directed to spray methods.

Paasche H3 in 1 Airbrushes were used in all work described in this report. The Airbrushes are small spray guns of a suction-feed type which make use of small amounts of material possible. The fact that they belong to the external-mix gun class made them especially useful for the purposes of this work.

A. Slurry Spraying

The slurry spraying was similar in principle to paint spraying, i.e., the operation represented only an application of a ready-made mixture or suspension at a given rate and in a definite pattern, and was not intended to bring about any synthetic chemical reaction at the time of spraying. Various slurries were prepared from G.E. luminescent grade cadmium sulfide, ground sintered mixtures of cadmium sulfide and indium sulfide prepared by the Electronic Research Division, and freshly precipitated CdS and CdS + In_2S_3 mixtures obtained by a reaction between cadmium salts and ammonium sulfide. Most work was done with the aqueous slurries, but some experiments were conducted with methanol, acetone, and their mixtures, and toluene as vehicles. 1" x 2" Pyrex glass plates were used as substrates in most tests, but mica sheet was slso used. The plates were cleaned with detergent, rinsed, kept for several minutes in chromic acid cleaning solution, rinsed and air-dried.

Generally, powdery and somewhat loosely-adhering deposits were obtained by this method. An improvement in texture and adhesion of deposit was noted when the temperature of the substrate was above $400^{\circ}C$. The freshly precipitated cadmium sulfide and mixtures with indium sulfide were found to

be superior to the other powders, probably due mainly to a finer particle size.

The resistance of deposits obtained by slurry spraying was high and no photovoltaic effect was noted. The chief operational problems, which also had an effect on the end product, were clogging of the gun nozzle by particles of the slurry, and the difficulty of keeping the powders in good suspension.

B. In-situ Reaction Methods

An ideal way to effect a reaction such as

$$CdCl_2 + (NH_4)_2S \longrightarrow CdS + 2NH_4Cl \qquad (A-6)$$
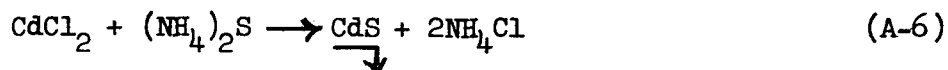
on a surface would be to bring the reactants to the surface and allow them to react only after they have reached the surface. This procedure would insure good "coverage" which is one of the qualities sought in this work. By growing in-situ, the crystals of cadmium sulfide might have a more desirable orientation. The process should produce a better-adhering deposit because of a tighter packing of smaller particles on the surface. The time required for reaction should be very short at room temperature and the reaction should be almost instantaneous at, say, 400°-600°C.

Several approaches were investigated in line with the above reasoning. The first obvious approach was to spray the balanced thiourea-EDTA solution onto a heated substrate, using nitrogen as a carrier gas. Accordingly, Pyrex plates were heated in a small laboratory muffle to 400°C and subsequently sprayed with the balanced solution. The resulting dense yellow deposits showed excellent uniformity and adhesion to the glass. They had a very high electrical resistance. Combinations of balanced solutions and slurries, when sprayed

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under similar conditions, resulted in good deposits, but their resistance was also too high to qualify them as good photovoltaic materials.

The next series of tests was conducted almost exactly as indicated in equation (A-6). Two spray-guns were employed simultaneously each using nitrogen as the carrier gas. The guns were focussed onto the 1" x 2" Pyrex plate from a distance of approximately 12". The cup of one gun contained the cadmium salt solution with no admixtures or with indium salt, depending on the experiment. The cup of the other gun contained various concentrations of ammonium sulfide, also depending on a given experiment. Four different heat cycles for the substrate were investigated:

(1) The substrate was at room temperature during spraying. Cadmium sulfide formed on the glass but it was not dense and did not form an adhering film on drying.

(2) The substrate was heated in the muffle to 400°C and was sprayed immediately after removal from the muffle. When the spray times were short, i.e. several seconds, the films produced were uniform and well-adhering. With longer spraying, nonuniform films were obtained in all cases when the plate became wet.

(3) The substrate was heated by focussing two 1,500 watt heat lamps onto it from a distance of about 1 foot. The surface temperatures attained in this fashion, measured by temperature sensitive color crayons, were about 350°C. The results of spraying onto Pyrex glass were comparable to those described under (2) above.

(4) The substrate was heated in the muffle and kept there during spraying. The range of temperatures investigated was 400° - 600° C. Generally, better continuity and adhesion of the deposits was obtained at higher temperatures. Under

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these conditions, and using indium chloride additions to
the cadmium chloride solution, it was possible to obtain
well-adhering continuous films showing resistance in the
range of 100-1000 ohms per square. A typical cycle, in
which deposits of this quality were obtained, was:

-5 min. preheat in muffle to about $500^\circ C$,

-10 sec. spray from two guns,

    a) 1.5 molar $CdCl_2$ solution,

    b) 22%$(NH_4)_2S$ solution;

- 1 min. heating;

-10 sec. spray from two guns,

    a) 0.5 molar $InCl_3$ solution,

    b) 22% $(NH_4)_2S$ Solution;

- 1 min. heating,

-10 sec. spray with $CdCl_2$ solution and $(NH_4)_2S$ Solution, as above.

- 1 min. heating, removal from muffle, cooling in air.

The resistance of these samples was much lower than those of
earlier attempts, but not as low as the vacuum deposited
material.

    As indicated earlier, the Airbrush spray-gun is of the
external mix type. Because of this feature, the rather
cumbersome procedure with two guns could be replaced by a
one-gun operation when hydrogen sulfide was used as a
carrier gas. In spite of the fact that mixing, and some
reaction, took place before the reagents reached the sub-
strate, most of the reaction took place on the heated
surface. It was quickly established that this method, i.e.
one-gun spraying using H_2S as carrier gas, was superior to
all methods described so far, at least to the extent that
these methods were explored. The resulting deposits were
highly reproducible in appearance, adhesion, continuity
and resistance measurements. The major problems in this

approach seemed to be avoidance of cadmium oxide formation under some experimental conditions and proper doping.

The formation of oxide was minimized by running nitrogen through the muffle, but it cannot be said that oxygen (air) was excluded completely - an occasional bluish glow inside the muffle at $600^{\circ}C$ indicated oxidation of hydrogen sulfide. No special effort was made to exclude the air which was inadvertently brought into the muffle when it was partly opened for spraying. Another source of oxygen in some experiments was the nitrate ion when cadmium nitrate was used. It was found that best results were obtained with cadmium chloride and this was the solution finally chosen for most work.

Despite the apparent good qualities of the deposits, as described above, no photovoltaic effect was noted. A wide range of concentrations of indium chloride in the cadmium chloride solution was investigated. "Sandwich spraying" was tried as above with a small dish with molten indium kept in the muffle to introduce some indium into the spray, but no photovoltaic effect could be observed despite the fact that the resistance of the films was brought down to about 10 ohms.

A radical improvement was achieved only after gallium was substituted for indium as a doping agent. A solution of gallium chloride was prepared by dissolving Ga_2O_3 in hydrochloric acid. A typical molar ratio of Ga:Cd in the spray solutions was 1:1500 to 1:400 or about 0.06 to about 0.25 mole %. Samples produced by this method on Pyrex plates showed photovoltaic effect up to 0.39 volts with a short circuit current of about 40 μ amp. The resistance of these samples was high, i.e. on the order of megohms. The deposition cycle was as follows:

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5 min. preheat at 600°C,

15 sec. spray with Ga-doped 1.5 molar $CdCl_2$ in stream of H_2S,

30 sec. heating at 600°C,

15 sec. spray, as above,

30 sec. heating at 600°C,

15 sec. heating as above,

1 min. heating at 600°C,

Cooling to room temperature in air.

SINTERING METHODS

It was thought that sintering might be one of the key processes in the successful deposition method described above. The fundamental process was, of course, the reaction between cadmium and gallium chloride and hydrogen sulfide, but intermittent and subsequent heating under nitrogen must also play an important role. It was established, for instance, that an additional application of cadmium chloride and subsequent 5 min. heating at 600°C in the atmosphere of nitrogen was very beneficial to the overall properties of the deposit. The additional cadmium chloride was applied by brushing a 0.2 molar aqueous solution on top of the cadmium sulfide deposit, drying in air and heating, as indicated above. It was believed that the excess cadmium chloride acted as a flux in the sintering procedure. Similar opinion was expressed by Thomsen[9] and Nicoll[15] in connection with all-sinter cadmium sulfide process.

An evaluation of Thomsen's and Nicoll's patents led to a series of experiments with various aqueous and alcoholic (methanol) slurries having the approximate composition:

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20 g CdS (luminescent grade),

2 g $CdCl_2 \cdot 2 \text{-} 1/2H_2O$

5-10 drops 0.1 molar $CuCl_2 \cdot 2H_2O$, $InCl_3$, or $GaCl_3$.

100 ml water or methanol.

The slurries were agitated vigorously just prior to application by brushing on clean and dry Pyrex plates (1x2"). The brushed-on material was allowed to air-dry and was subsequently baked in an atmosphere of nitrogen at $600^{\circ}C$ for varying periods of time ranging from 5 min. to 30 min. Relatively low-resistance material was obtained in this way, but the uniformity was poor. The photovoltaic effect (0.1 to 0.3 volt) was observed only in narrow bands (about 2-3 mm wide) around the periphery of the specimen. The formation of such bands was obviously connected with the drying technique, but it was not possible to improve the uniformity of the drying pattern in the time allotted for this study.

Generally, it might be said that the use of indium and gallium in place of copper (the latter is used in Thomsen's and Nicoll's patents) was demonstrated to be possible in the sintering procedure. The sintering method produced low-resistance photovoltaic material. The uniformity of the sintered material, as far as could be determined in this limited study, was not satisfactory.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDIES

There is enough merit in the approaches to the problem of deposition of doped cadmium sulfide by methods other than vacuum deposition to consider further study of such approaches. This conclusion is borne out by the en-

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couraging experimental results obtained with the spray method, in particular, with the direct $CdCl_2 + H_2S + GaCl_3$ spray method. The spadework done with the solution-immersion methods, in particular on the copper foil substrate, might be less spectacular in results produced, but they also showed some promise.

Perhaps, most attention should be devoted to the spray techniques and/or combination of such techniques with sintering. Should the high temperature required for sintering (about $600^{\circ}C$) be a prohibitive factor, as it might well be with organic substrates, then spraying alone and/or longer heating at lower temperatures should be studied.

8. WORK PLANNED FOR NEXT QUARTER

In the next quarter, work will continue in general along the lines discussed in this report. The series of electrical and optical measurements described in Section 4 will continue. Greater emphasis will be placed on evaporated films. Film substrates will be emphasized in the chemical approach. The correlation between film cell quality and evaporant will be studied very carefully. The recent modifications in the evaporator will greatly aid this phase, because we shall no longer be bound to the nonuniformities of single crystal chips. The film structure studies will continue as a major effort. More sunlight efficiency measurements will be made.

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10. PERSONNEL

Time devoted to this project by principal technical personnel and others in the period April 1, through June 30, 1963, follows:

		Hours
W. J. Deshotels	Project Scientist	484
F. Augustine	Senior Chemist	504
A. E. Carlson	Senior Physical Chemist	355
J. Koenig	Senior Chemical Engineer	294
M. P. Makowski	Senior Chemist	50
Others		1525
	Total	3212

11. EXPENDITURES

Actual costs, October 1, 1962 through June 30, 1963 $ 91,200.

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Attention: C. A. Escoffery   1

National Cash Register Company
Physical Research Department
Dayton 9, Ohio
Attention: R. R. Chamberlin   1

CLEVITE CORPORATION   **ELECTRONIC RESEARCH DIVISION**

Aeronautical Systems Division
Wright-Patterson AF Base, Ohio
Attention: Mr. James L. Mattice, ASRCN-22   1

Aeronautical Research Laboratories
Office of Aerospace Research, USAF
Wright-Patterson AF Base, Ohio
Attention: Mr. D. C. Reynolds, ARX
          Chief, Solid State Physics Research Laboratory   1